

VOL. 23

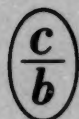
NO. 8

AUGUST 1953

JOURNAL OF
**GENERAL
CHEMISTRY**
of the USSR

ЖУРНАЛ ОБЩЕЙ ХИМИИ
(ZHURNAL OBSHCHEI KHIMII)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU



THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

Volume XXIII, No. 8

August, 1953

(A Publication of the Academy of Sciences of the U. S. S. R.)

IN ENGLISH TRANSLATION

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152 West 42nd Street

New York 18, N. Y.

Printed in the United States

Annual subscription	\$95.00
Single issue	20.00

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FOURTH - LAST SECTION

CHROMIUM DIOXIDE--PREPARATION, PROPERTIES, AND ENTHALPY OF FORMATION

S.M. Ariya, S.A. Shchukarev, and V.B. Glushkova

Chromium oxides with compositions intermediate between Cr_2O_3 and CrO_2 have been the subject of many researches. Preparations with such compositions are obtained either by decomposing chromyl chloride, CrO_2Cl_2 [1,2,3,4], by decomposing chromic anhydride [5,6,7,8,9,10], or by oxidizing hydrated chrome oxide using oxygen [11,12,13]. Certain authors believe that these preparations have variable composition phases, $\text{CrO}_{2.6}$ – $\text{CrO}_{2.2}$ and $\text{CrO}_{1.9}$ – $\text{CrO}_{1.7}$ [14], others that a definite compound, CrO_2 , exists.

The magnetic properties of these oxides were also studied; it was found that some of them were ferromagnetic, but even in this regard data of various investigators are contradictory [4,5,15]. Results of roentgenographic investigation likewise either did not lead to definite conclusions on the nature of the intermediate chromium oxides or showed that the authors were dealing with a mixture of several crystalline phases [6].

Synthesis of Chromium Dioxide.

Assuming that the different results of the several investigators could be explained by the fact that the authors were dealing with samples obtained under conditions where they were not at thermodynamic equilibrium with the products of decomposition, we decided to study the process of decomposing chromium anhydride under the condition of a high oxygen pressure.

In this it was found that decomposition of chromium anhydride at a temperature of 420–450°C and at an oxygen pressure of 200–300 atmospheres, produced a black colored substance, the composition of which was the same in all experiments, and corresponded to the formula $\text{CrO}_{1.98}$, i.e., was very close to the formula of chromium dioxide.* Analysis was performed both by determining the amount of weight loss on decomposition by calcination to 800°, and also by decomposition in a vacuum with subsequent measurement of the oxygen volume separated thereby. Comparison of results obtained by both methods shows that the compounds prepared under the stated conditions were anhydrous.

Roentgenographic Investigation

A sample, held for a long time at 450° with an oxygen pressure of 280 atmospheres, gave a powder picture, which, as is apparent from Figure 1 ($\text{CrO}_{1.98}$), seems sufficiently clear for its indication. In Table 1 are given the interplanar spacing values found by us and the results of identification according to the Biström curves. This identification shows that $\text{CrO}_{1.98}$ forms a lattice with tetragonal syngony. The elementary cell parameters were: $a = 4.394 \pm 0.015$, $c = 5.77 \pm 0.02$, $c/a = 1.31$. The density of this preparation measured pycnometrically in cyclohexane was found to be 4.90 g/cm³ (25°C). If we assume that the elementary cell contains 4 CrO_2 "molecules", then the roentgenographic density appears equal to 4.97 g/cm³, which is in good agreement with the value found pycnometrically.

Magnetic Properties

Measurement of magnetic susceptibility, performed by the "cylinder method", showed that at room temperature the magnetic susceptibility value depended on field strength (Figure 2), i.e., chromium dioxide is ferromagnetic.

* It is pointed out that we have a case of structure defects here. However, the closeness of this formula to the CrO_2 does not deprive us of the possibility of calling this compound the dioxide and of using the formula CrO_2 in qualitative discussion, similar to the fact that they write "FeO" although a stable phase of this composition, as is known, does not exist.

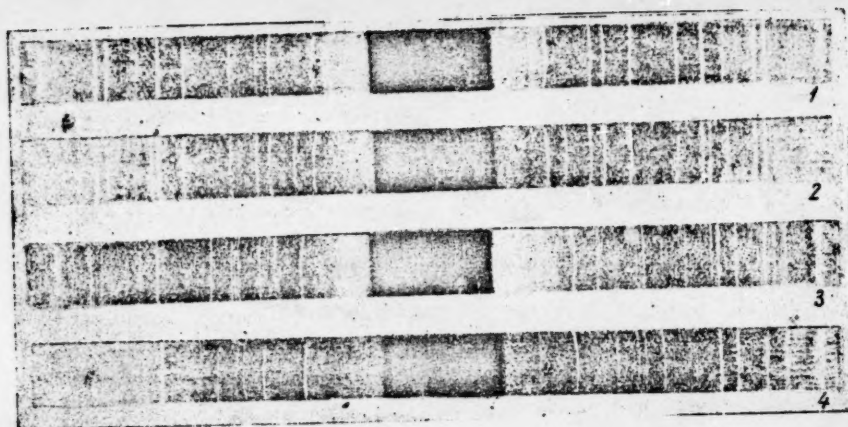


Fig. 1. Powder pictures of chromium oxides of varying composition: 1) $\text{CrO}_{1.50}$, 2) $\text{CrO}_{1.42}$, 3) $\text{CrO}_{1.35}$, 4) $\text{CrO}_{1.28}$. The Roentgenograms were taken with a camera having a diameter of 57.3 mm, on chromium radiation with a vanadium filter. The sample diameter was 1 mm. Potential was 25 kilovolts, current strength 20 milliamperes, exposure 3 hours.

TABLE 1

Results of Roentgenographic Identification

Line number	Interplanar spacing, A	Intensity (visual)	Index
1	3.08	Strong	110
2	3.41	Average	102
3	2.19	Weak	200
4	2.11	Average	112
5	1.97	Weak	210
6	1.62	Strong	113
7	1.55	Strong	220
8	1.44	Average	203
9	1.390	Strong	310
10	1.311	Strong	114

The Curie temperature was found to equal 115°C , which is close to the value given by Zhukov [3] for one of the products from decomposing chromium anhydride (having the composition $\text{CrO}_{2.2}$). It should be noted that the particular magnetic property of chromium dioxide (ferromagnetism) in the series of dioxides of elements of the 1st inserted decade corresponds to a lattice structure peculiarity in this very series. Titanium, vanadium, and manganese dioxide (not ferromagnetic) have an elementary cell with similar values for parameter a (TiO_2 4.58, VO_2 4.54, CrO_2 4.394, MnO_2 4.398), but the value of parameter c for CrO_2 is approximately twice as large as for the dioxides of its neighboring elements [16] (TiO_2 2.95, VO_2 -2.88, CrO_2 -5.77, MnO_2 -2.867).

Bete and Sleiter [17] showed that the condition for appearance of ferromagnetism was the presence of par-

ticles with incomplete electronic levels having large values of the second quantum number, and a large value for the ratio of the distances between centers of the particles and their radii.

The first condition is satisfied, evidently, for all the dioxides; as regards the ratio just mentioned, it has the largest value for CrO_2 :

Ratio of distance between ion centers to ion radius	TiO_2	VO_2	CrO_2	MnO_2	MoO_2	WO_2
	2.30	2.36	3.92	2.75	2.05	2.03

Results of measuring magnetic susceptibility at temperatures above the Curie point are given in Table 2, where they are compared with values calculated from assuming that CrO_2 was actually a dioxide, or from assuming that we were dealing here with chromates of trivalent chromium ($\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$).

The data of Table 2 show that the experimental magnetic susceptibility values for $\text{CrO}_{1.35}$ are closer to values calculated based on assuming the presence of tetravalent chromium ions in the lattice of this compound, i.e., we may consider that $\text{CrO}_{1.35}$ actually is a dioxide, and not a mixed oxide.

TABLE 2

Temperature, °C	Magnetic susceptibility per mole		
	Value		
	Experimental	Calculated for CrIVO_2	Calculated for $\frac{1}{3} \text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$
225	8040	9100	11400
264	5800	6700	8400
320	4100	4900	6200

It is pertinent to note that the magnetic susceptibility of molybdenum and tungsten dioxide, in contrast to the susceptibility of chromium dioxide, has a much lower theoretical value; this indicates the presence of bonds between the metallic ions. Probably, this difference may be set in relation to the larger enthalpy of sublimation value for molybdenum and tungsten (155 kcal for Mo and 210 kcal for W) as compared with the enthalpy of sublimation of chromium (89 kcal [18].)

Thermal Decomposition under Conditions Close to Equilibrium

For preliminary exploration of the width of the region of homogeneity for chromium dioxide, a series of experiments was set up decomposing chromium anhydride at 450°C at various oxygen pressures (duration of heating amounted to 8 hours in all cases).

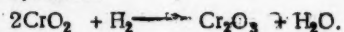
The composition of the preparations obtained depended on the oxygen pressure in the following manner:

O ₂ pressure, atm.	280	100	95	90	75
Composition:	$\text{CrO}_{1.98}$	$\text{CrO}_{1.98}$	$\text{CrO}_{1.92}$	$\text{CrO}_{1.92}$	$\text{CrO}_{1.92}$

Roentgenograms of products having the gross compositions $\text{CrO}_{1.92}$ and $\text{CrO}_{1.98}$ showed the presence of a Cr_2O_3 phase and a $\text{CrO}_{1.98}$ phase; here the interplanar distance in these latter seemed independent of pressure (Figure 1). We may thus conclude that $\text{CrO}_{1.98}$ does not have a perceptible region of homogeneity. It is of interest also in this connection that chromium dioxide occupies a particular place in the series of dioxides of the elements of the 1st inserted decade. Figure 3 presents dioxide existence regions for elements which neighbor chromium.

Enthalpy of Formation of Chromium Dioxide

The reaction most suitable for use in a calorimeter is the reaction reducing chromium dioxide by hydrogen, occurring according to the equation:



This process was conducted at a hydrogen pressure of 20 atmospheres and was initiated using a heated spiral of fine platinum wire, placed in the chromium dioxide powder. To measure the change in temperature a resistance thermometer was used as one of the legs of a Wheatstone bridge.

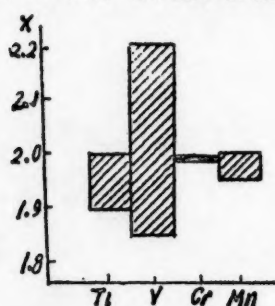


Fig. 3. Region of homogeneity for dioxides of elements in the 1st inserted decade.

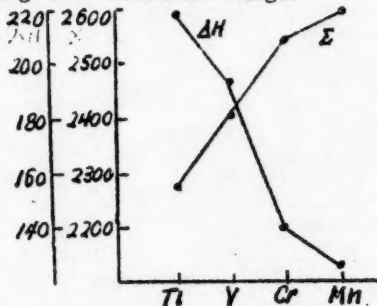


Fig. 4. Course of energy total for removing four electrons and the enthalpy of sublimation, Σ , for Ti, V, Cr, and Mn; and course of enthalpy of formation ΔH (kcal/mole) for corresponding dioxides.

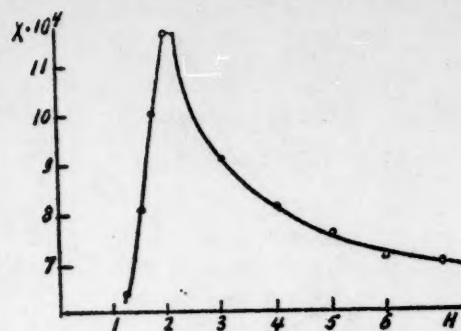


Fig. 2. Dependence of magnetic susceptibility, χ , of the $\text{CrO}_{1.98}$ preparation on field strength, H , (in arbitrary units) at room temperature.

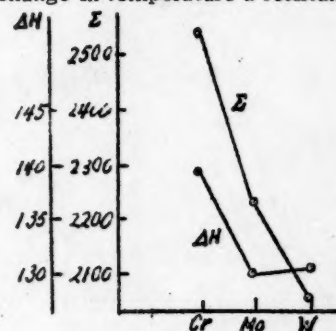


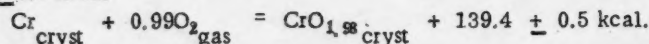
Fig. 5. Course of energy total for removing four electrons and enthalpy of sublimation, Σ , for Cr, Mo, and W, and course of enthalpy of formation ΔH (kcal/mole) for corresponding dioxides.

The "water value" of the calorimetric bomb was determined by measuring the temperature rise which corresponded to introducing a determined quantity of energy into the bomb; it was measured potentiometrically.

At 25° C for the reaction:



a change in enthalpy equal to -59.8 ± 0.5 kcal was found. From this, using an enthalpy of formation of -273 kcal, and an enthalpy of formation of liquid water equal to -68.37 kcal [18], the enthalpy of formation of chromium dioxide was found to be -139.4 ± 0.5 kcal.



It was shown by one of us [19] that the trend in heat of formation of binary compounds along a series of analogous compounds is often contrary to the trend in sum of corresponding valences, or in the sum of ionization potential and enthalpy of sublimation for the corresponding simple bodies to free atoms.

Figure 4 shows that this relation may be very clearly observed in the TiO_2 - MnO_2 series.

Matters are otherwise on transition from chromium to its analogs in the supplemental subgroup of group VI. Figure 5 shows that the converse relationship stated above does not exist in this case.

SUMMARY

1. Decomposition of chromium anhydride at temperatures of 420-450° C and oxygen pressures of 200-300 atmospheres leads to formation of anhydrous chromium dioxide.
2. Chromium dioxide has a tetragonal structure. The elementary cell dimensions are $c = 5.77 \pm 0.02$ Å, $a = 4.394 \pm 0.15$ Å, ($c/a = 1.31$), and contains 4 atoms of chromium and 8 oxygen atoms.
3. Chromium dioxide evidently does not have a very perceptible region of homogeneity.
4. Chromium dioxide is ferromagnetic; the Curie temperature was 115° C. The magnetic susceptibility above the Curie temperature was close to that calculated assuming that $\text{CrO}_{1.98}$ contains Cr^{4+} ions, i.e., that it was actually a dioxide, and not a mixture of oxides ($\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$).
5. The enthalpy of formation of chromium dioxide, found by calorimetric measurement of change in enthalpy during the reduction reaction with hydrogen to chromium oxide, was equal to -139.4 ± 0.5 kcal/mole:

$$\text{Cr}_{\text{cryst}} + 0.99\text{O}_{2\text{gas}} = \text{CrO}_{1.98}\text{cryst} + 139.4 \pm 0.5 \text{ kcal}$$
6. The trend in enthalpy of formation of TiO_2 , VO_2 , CrO_2 , and MnO_2 is converse to the trend in the sum of enthalpy of sublimation for the corresponding metals and the energy for removing four electrons from their atoms. The trend in enthalpy of formation of chromium, molybdenum, and tungsten dioxides did not show this converse relation.

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Received March 27, 1953.



REACTIONS IN FUSED NITRATES AND NITRITES OF METALS
OF THE FIRST AND SECOND GROUPS OF THE D. I. MENDELEEV PERIODIC SYSTEM

VI. INVESTIGATION OF THE TERNARY SYSTEM
RUBIDIUM NITRATE - POTASSIUM NITRATE - CADMIUM NITRATE

P. I. Protsenko and N. P. Popovskaya

It was previously reported [1] that potassium nitrate reacts with cadmium nitrate in a melt to form a complex compound, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$, whose melting point is 199.5° . The clearly evident chemical affinity between the above noted components was observed not only in the binary, but also in a ternary system in presence of lithium nitrate as a third component. The present investigation has as a purpose exploration of the nature of reaction between rubidium and cadmium nitrates in the molten state, and also study of their effect on the previously described chemical compound.

The marked similarity, with regard to most physico-chemical properties, between potassium and rubidium nitrates forms the basis for predicting the nature of the relationship of rubidium nitrate to cadmium nitrate. This must be analogous to the relationship of potassium nitrate to cadmium nitrate, i.e., even in this case we should expect appearance of chemical reaction between the stated components. Here we should assume that the thermal stability of the proposed compound, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$, would be greater than the thermal stability of the compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$.

The experimental investigation performed, as will be shown below, confirmed our assumptions. Rubidium nitrate actually enters into chemical reaction with cadmium nitrate and forms the complex compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$ with it. As regards the thermal stability of this compound, judging from its melting point, it seems somewhat less than that of the compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$.

EXPERIMENTAL

Binary systems. The equilibrium diagram for the binary system potassium nitrate - cadmium nitrate, which corresponds to one side of the triangular diagram of the above stated ternary system, has been previously described by one of us [1]. Investigation of the potassium nitrate - rubidium nitrate binary system, also corresponding to one side of the triangular diagram, showed that rubidium nitrate and potassium nitrate, in consequence of their marked similarity with regard to most physico-chemical constants, and in particular the very small difference in their atomic radii (rubidium 2.51 Å, potassium 2.38 Å), form a continuous series of solid solutions. The liquidus curve of this system is a smooth crystallization branch, bowed slightly toward the composition axis. The crystallization curve minimum is very weakly expressed. It corresponds to the composition: * 35 mole-% potassium nitrate and 65 mole-% rubidium nitrate, with a m.p. of 296.5° (Fig. 1.).

The equilibrium diagram for the rubidium nitrate - cadmium nitrate system was studied for the first time by us. The liquidus curve for this system has three crystallization branches: cadmium nitrate, the chemical compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$, and rubidium nitrate. The first eutectic point corresponds to the composition: 58.5% cadmium nitrate and 41.5% rubidium nitrate with a 167° m.p.; the second: 37% cadmium nitrate and 63% rubidium nitrate with a 172° m.p. The maximum on the chemical compound curve corresponds to a m.p. of 184° (Fig. 1).

* Composition data are always given in mole percent throughout.

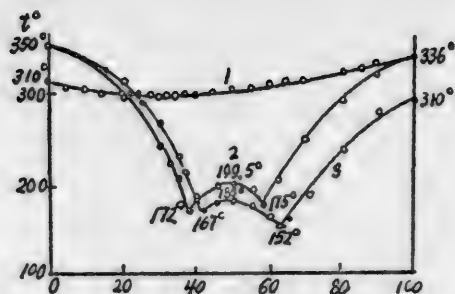


Fig. 1. Binary systems. 1— $\text{RbNO}_3\text{--KNO}_3$;
2— $\text{Cd}(\text{NO}_3)_2\text{--KNO}_3$; 3— $\text{Cd}(\text{NO}_3)_2\text{--RbNO}_3$.

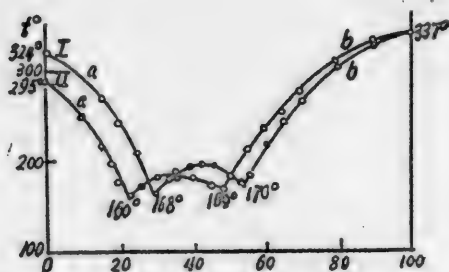


Fig. 3. Sections through ternary system:
I) $85\% \text{ Cd}(\text{NO}_3)_2 + 15\% (\text{RbNO}_3)_2 \rightarrow \text{KNO}_3$;
II) $75\% \text{ Cd}(\text{NO}_3)_2 + 25\% (\text{RbNO}_3)_2 \rightarrow \text{KNO}_3$;
a) $\text{Cd}(\text{NO}_3)_2$ branch; b) $\text{KNO}_3 + \text{RbNO}_3$ branch.

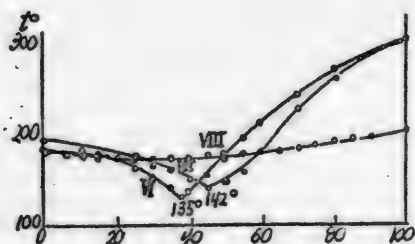


Fig. 5. Sections through ternary system:
VI) $60\% \text{ Cd}(\text{NO}_3)_2 + 40\% (\text{KNO}_3)_2 \rightarrow (\text{RbNO}_3)_2$;
VII) $67\% \text{ Cd}(\text{NO}_3)_2 + 33\% (\text{KNO}_3)_2 \rightarrow (\text{RbNO}_3)_2$;
VIII) $\text{Cd}(\text{NO}_3)_2 \cdot \text{RbNO}_3 \rightarrow \text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$.

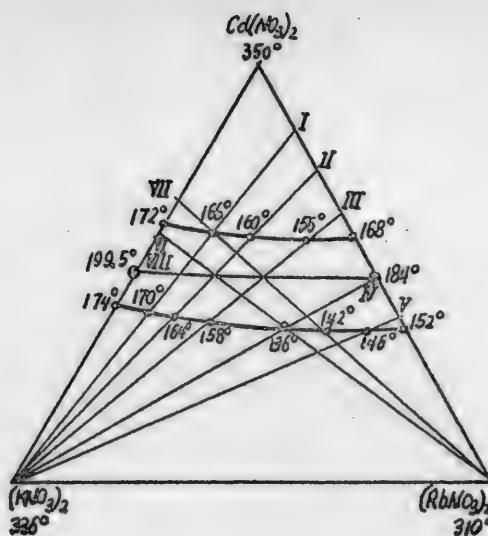


Fig. 2. Direction of sections in the ternary system.

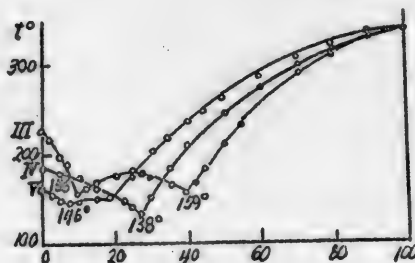


Fig. 4. Sections through ternary system:
III) $65\% \text{ Cd}(\text{NO}_3)_2 + 35\% (\text{RbNO}_3)_2 \rightarrow (\text{KNO}_3)_2$;
IV) $50\% \text{ Cd}(\text{NO}_3)_2 + 50\% (\text{RbNO}_3)_2 \rightarrow (\text{KNO}_3)_2$;
V) $40\% \text{ Cd}(\text{NO}_3)_2 + 60\% (\text{RbNO}_3)_2 \rightarrow (\text{KNO}_3)_2$.

Ternary system. The ternary system liquidus surface was investigated along eight sections, the directions of which are shown in Figure 2. Five sections were investigated from the cadmium nitrate—rubidium nitrate side of the triangle with potassium nitrate as a vertex; two sections were studied along the cadmium nitrate—potassium nitrate side with rubidium nitrate as a vertex; the eighth section passed through the chemical compound field.

Equilibrium diagrams for sections I, II, III, IV, and V enable determining lines which bound the cadmium, potassium, and rubidium nitrate crystallization fields.

Sections VI and VII are controls. Section VIII enables establishing the uniformity of the chemical compound field.

Transition points on section equilibrium diagrams and also the corresponding melting points and component compositions are given in the table.

TABLE

Section No.	$\text{Cd}(\text{NO}_3)_2$ mole %	KNO_3	RbNO_3	Transition point melting temp.
I	a*	59	11	166
	b*	38.7	7.3	170
II	a*	59	19	160
	b*	39	13	164
III	a*	58.5	31.5	156
	b*	38.5	21.5	159
IV	36.5	27	36.5	138
V	38	8	54	146
VI	37	25	38	155
VII	36.5	16.5	47	142
VIII	No transition point			
	a* — composition of first transition point			
	b* — composition of second transition point			

Liquidus curves for the sections are given in Figs. 3, 4, and 5. Experimental data for the ternary system are generalized into a projected isothermal ternary equilibrium space diagram. The isotherms are generally spaced at 50°; in the chemical compound region they are at 10° (Fig. 6).

It can be seen from Fig. 6 that the rubidium nitrate—cadmium nitrate—potassium nitrate ternary system liquidus surface has three crystallization fields: the isomorphic mixture of rubidium and potassium nitrates covering 60.93% of the crystallization area, that of the chemical compounds $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$, covering 22.61% of the crystallization area, and cadmium nitrate which covers 16.46% of the crystallization area.

We consider now the chemical compounds $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$, which form a single crystallization field. Evidently, rubidium and potassium nitrates, being isomorphic [2], on reacting with cadmium nitrate in the melt form isomorphic chemical compounds— $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$, respectively, which on mixture with one another when molten also give a continuous series of isomorphic mixtures (solid solutions). The shape of the Section VIII liquidus curve (Fig. 5), starting from the chemical compound point on the potassium nitrate—cadmium nitrate side of the triangular diagram and ending at the chemical compound composition point on the rubidium nitrate—cadmium nitrate side, confirms our discussion.

Because a single field of isomorphic mixtures of the above stated chemical compounds is formed, the ternary system equilibrium diagram has an unusual appearance,—the diagram has a "belt", formed by isomorphic mixtures of the compounds $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$ (Fig. 6).

In addition, investigation of the above stated system showed that potassium and rubidium nitrates display a clear tendency to react chemically with cadmium nitrate in melts. Here the tendency toward complex formation is more strongly shown with potassium nitrate than with rubidium nitrate; this follows by comparing the binary system equilibrium diagrams (Fig. 1) and the thermal stability of the given compounds.

Because cadmium nitrate decomposes at temperatures of 318–324°, i.e., below the melting point given in handbook literature*, the melting points of mixtures of components in the cadmium nitrate—rubidium nitrate binary system were measured from 15 to 100% rubidium nitrate. At smaller contents of the latter, the salt melt decomposed with nitrogen dioxide evolution and cadmium oxide formation.

It is characteristic that a transition of the molten salts into the glassy state took place with an enormous viscosity increase in the above stated binary system at a definite rubidium nitrate—cadmium nitrate concentration. Transition of the melt into the glassy state was also observed in the ternary system. This phenomenon was repeatedly observed by us in our earlier investigation of systems of nitrates of metals in the first and second groups of the D.I. Mendeleev periodic table [1, 2, 3], and moreover, was described by A.P. Rostkovsky [4] who investigated the calcium nitrate—potassium nitrate binary system.

* The melting point given in handbook and periodical literature for cadmium nitrate does not correspond to actuality; this will be shown by us in one of these papers.

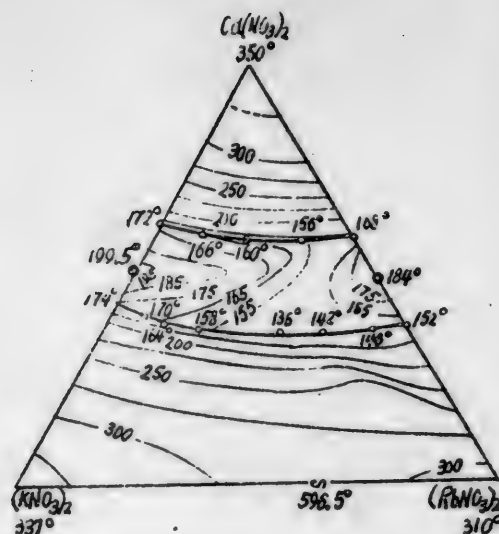


Fig. 6. Base projection of ternary system crystallization surface.

In all the cases we previously described, appearance of the glassy state in fused nitrate components was observed only at definite concentrations of the latter, and was always associated with an enormous increase in viscosity. Doubtless, in similar cases, there will be a genetic viscosity relationship between components in the melt having chemical affinity. Exploration of this relationship particularly represented one of the problems in the study performed by us.

SUMMARY

1. It was shown by a visual-polythermal method of physico-chemical analysis that rubidium nitrate forms the chemical compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$, melting at 184° , when fused with cadmium nitrate.

2. It was shown that the thermal stability of the complex compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$ was less than that of the compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$ previously prepared by us.

3. The liquidus surface of the rubidium nitrate-cadmium nitrate-potassium nitrate ternary system was studied, and formation of the above named chemical compounds was confirmed by the presence of a corresponding crystallization field within the ternary system.

4. The isomorphism of the chemical compounds $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$ is discussed, based on the nature of their crystallization field.

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Received March 17, 1953.

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* See Consultants Bureau Translation, p. 1357.

** See Consultants Bureau Translation, p. 1421.

SODIUM HEXAMETAPHOSPHATE

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In many respects the oxygen compounds of phosphorus are similar to carbon and silicon compounds, especially in regard to their ability to form polymers. A large number of such polymers are known of metaphosphoric acid, or more accurately, of its salts, of which sodium hexametaphosphate has obtained practical application.

Jones [1] recently gave a method for analyzing a mixture of phosphoric acids, enabling a better approach to the investigation of this unusual product. He determines hexametaphosphate, ortho- and pyrophosphate separately and the sum of tri- and tetrapolyphosphates by difference.

The hexametaphosphate is precipitated quantitatively as barium metaphosphate by barium chloride at a pH of the order of 2.5-3, and then ortho-, pyro-, and polyphosphates are precipitated by neutralizing to phenolphthalein. Trimetaphosphate does not precipitate under these conditions, and is determined in the filtrate. Ortho- and pyrophosphates are determined in separate samples after separating the hexametaphosphate [2], the latter by precipitation at pH 4.1 with manganese chloride in presence of acetone. In each of the components, phosphorus is determined by ammonium molybdate, as in determining total phosphorus. Sodium hexametaphosphate was obtained from monosodium phosphate. After dehydration, the monosodium phosphate melts, forming a mobile liquid. To prepare sodium hexametaphosphate, it is necessary to chill this melt rapidly.

Table 1 gives composition constants for products obtained in the temperature interval 620-900° on heating after fusing the starting product for from 10 minutes to 6 hours. The initial product did not fuse below 600°. Heating time and temperature in the stated limits did not affect the yield; this agrees with data of Postnikov and Bronnikov [3]. Also, chilling conditions have no affect, when varied from room temperature to that of solid carbon dioxide (-78.5°). The thermograms were taken with a heating speed of 4° per minute.

TABLE 1

Length of expt. (min.)	Temp. of expt.	P ₂ O ₅ content of product obtained (%)	Composition of product obtained (%)	
			Hexameta-phosphate	Trimeta-phosphate
30	620-630°	69.5	90.1	9.9
30	720-730	69.5	90.2	9.8
30	820-830	69.4	90.4	9.6
30	870-900	69.5	90.3	9.7
10	620-630	69.3	90.1	9.9
30	620-630	69.5	90.1	9.9
60	620-630	69.4	90.2	9.8
180	620-630	69.5	90.4	9.6
30	870-900	69.5	90.3	9.7
120	870-900	69.4	90.4	9.6
240	870-900	69.4	90.7	9.3
360	870-900	69.2	90.3	9.7

TABLE 2

Temperature of the melt	of cooling the melt	P ₂ O ₅ content in product obtained (%)	Composition of product obtained (%)	
			Hexameta-phosphate	Trimeta-phosphate
620-630°	*	69.5	90.1	9.9
620-630	0	69.5	90.2	9.8
870-900	*	69.5	90.3	9.7
870-900	0	69.4	90.3	9.7
870-900	-78.5	69.3	90.1	9.9

* Room temperature

Dehydration of monosodium phosphate crystal hydrate takes place in two stages: in the first, a molecule of water splits off between 33-43°, and the second in the 70-80° interval (Fig. 1).

More accurate transition points indicate that these temperatures are equal to 43.5 and 78.5°.

When the second water molecule has split off, a saturated solution of anhydrous monosodium phosphate is

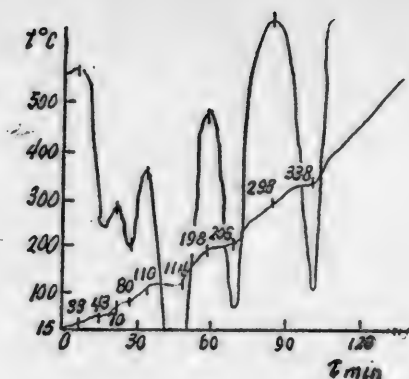


Fig. 1. Thermogram for aqueous monosodium phosphate.

formed which on further heating begins to boil at 114°. Subsequently, monosodium phosphate decomposes forming acid pyrophosphate at 198 - 206°. Metaphosphate then is formed in the 298 - 338° interval. Initial melting takes place at 610°.

Sodium metaphosphate undergoes transformation on heating and forms polymetaphosphates. It can be seen from Fig. 2 that two endothermal effects take place in the 500 - 600° temperature interval; these are very small in magnitude. To study this process, we increased the differential trace sensitivity; this showed two endothermal transitions in the 500-600° interval. The endothermal effects in Fig. 1 in the 512-560° and 300-608° intervals are connected with dehydrating the hydrated crystals, because they are completely absent in heating the anhydrous product.

Sodium hexametaphosphate, obtained by heating monosodium phosphate in a platinum dish at 630° and containing 90.1% hexametaphosphate and 9.9% trimetaphosphate, was crushed to powder in a porcelain mortar, and heated in a porcelain crucible. In view of the comparatively low specific volume of sodium hexametaphosphate compared to magnesium oxide, titanium dioxide was used as a standard.

The endothermal effect beginning at 322° corresponds to transition of hexametaphosphate into trimetaphosphate.

Analysis of samples heated to 330° for a period of three-five minutes showed that sodium hexametaphosphate was quantitatively transformed into sodium trimetaphosphate; consequently, this effect is not caused, for example, by sintering. At this temperature, sodium hexametaphosphate softens and can be drawn into threads like glass.

On longer heating at this temperature, instead of sodium trimetaphosphate as the main product, other water-insoluble metaphosphates are obtained; the quantity of these increases with increased time of heating. This procedure is suitable for preparing pure trimetaphosphate. At this temperature two processes take place; the first is completed rapidly and corresponds to transition of sodium hexametaphosphate into trimetaphosphate; the second takes place much more slowly and corresponds to transition of trimetaphosphate into other water-insoluble metaphosphates. The endothermal effect in the 614 - 630° interval in Fig. 3, corresponds to fusion of sodium trimetaphosphate, which contained, according to the temperature conditions, some polymetaphosphate as an impurity.

Sodium hexametaphosphate does not have a specific melting point and is converted into sodium trimetaphosphate. A number of authors report melting points in the 610 - 640° interval (Bronnikov [4]). Analogous transitions take place with uncrushed sodium hexametaphosphate, although in this case the process occurs much more slowly. Sodium hexametaphosphate hydrolyses markedly, particularly at higher temperatures. For hydrolysis we took a product containing 90.4% sodium hexametaphosphate and 9.6% trimetaphosphate. Hydrolysis of 1 and 2.5% aqueous solutions was performed at 60 and 100°. The samples for analysis were first taken after 24 hours at 60° and after 2 hours at 100°. Hexametaphosphate and trimetaphosphate were determined in the hydrolyzed products. Total remaining phosphate was determined by the difference between total P_2O_5 and the sum of hexametaphosphate and trimetaphosphate (Tables 3 and 4).

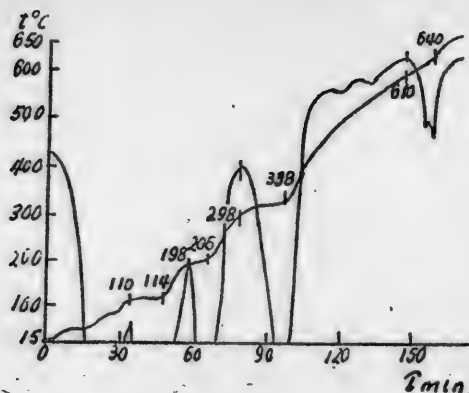


Fig. 2. Thermogram for monosodium phosphate.

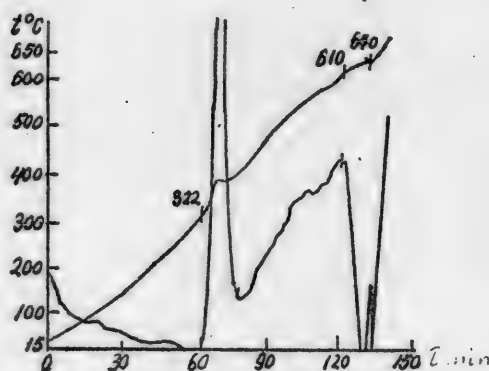


Fig. 3. Thermogram for hexametaphosphate.

TABLE 3

Hydrolysis of 1 and 2.5% Sodium Hexametaphosphate Solutions at 60°

Time of holding sample for analysis (hrs.)	1% solution		2.5% solution	
	Obtained (%)		Obtained (%)	
	Hexameta-phosphate	Trimeta-phosphate	Hexameta-phosphate	Trimeta-phosphate
—	90.4	9.6	90.4	9.6
24	88.2	11.7	88.2	11.1
48	84.4	14.7	82.6	12.6
72	—	—	77.1	14.5
96	75.3	17.5	—	—
120	—	—	66.5	19.0
144	68.1	19.8	—	—
168	—	—	60.0	21.8
192	62.0	20.8	—	—
216	—	—	55.2	24.1

TABLE 4

Hydrolysis of 1 and 2.5% Sodium Hexametaphosphate Solutions at 100°.

Time of holding sample for analysis (hrs.)	1% solution		2.5% solution	
	Obtained (%)		Obtained (%)	
	Hexameta-phosphate	Trimeta-phosphate	Hexameta-phosphate	Trimeta-phosphate
—	90.4	9.6	90.4	9.6
2	66.0	16.8	64.5	18.3
4	46.9	21.0	42.6	22.5
6	28.2	27.0	25.1	27.4
8	14.3	29.7	9.2	29.9

Sodium hexametaphosphate hydrolyzes in two directions in aqueous solutions. Some of it depolymerizes into sodium trimetaphosphate; this is shown by the increasing quantity of trimetaphosphate; some of it goes to ortho- and other phosphates; this agrees with Bell's conclusions [5].

The hydrolysis rate is sharply dependent on temperature; however, the data obtained do not agree with data of Bronnikov and Bell. Thus, the hydrolysis rate as found by us, particularly at 100°, was much smaller (Table 3 and 4 and Figs. 4 and 5). In these two figures, the percent content of phosphoric anhydride, present as the sodium hexameta-, trimeta-, or total residual phosphate, is plotted along the ordinate; time is plotted along the abscissas axis.

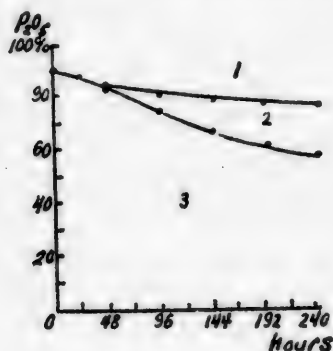


Fig. 4. Hydrolysis of a 1% hexametaphosphate solution at 60°.

- 1) Trimetaphosphate; 2) total phosphates;
3) hexametaphosphate.*

* No curve 3 appears in the original. Publisher.

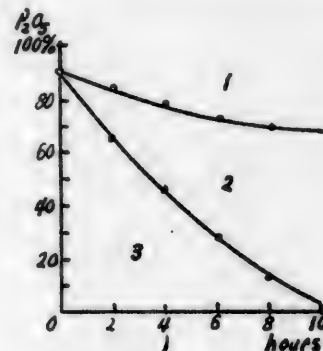


Fig. 5. Hydrolysis of a 1% hexametaphosphate solution at 100°.

- 1) Trimetaphosphate; 2) total phosphates;
3) hexametaphosphate.*

* No curve 3 appears in the original. Publisher.

The curves give percent phosphate content present with time in the form of sodium hexametaphosphate, sodium trimetaphosphate, and the sum of the other phosphates.

SUMMARY

1. The condition for preparing sodium hexametaphosphate from monosodium phosphate is heating at 620–630° for a 15–30 minute period with rapid subsequent cooling of the melt to room temperature.
2. Pure sodium trimetaphosphate was obtained by heating powdered sodium hexametaphosphate at 330° for a period of three–five minutes.
3. Sodium hexametaphosphate does not have a fixed melting point, because on heating it softens gradually and is transformed into the trimetaphosphate at 330°.
4. Thermographic investigations were performed on monosodium phosphate and on sodium hexametaphosphate over the 15–650° interval.

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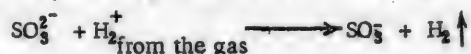
Received November 17, 1952

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OXIDATION OF AQUEOUS SODIUM SULFITE SOLUTIONS BY POSITIVE GASEOUS HYDROGEN, HELIUM, AND OXYGEN IONS

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The method of oxidizing aqueous sodium sulfite solutions by positive gaseous ions was proposed by V. I. Pavlov in the development of his studies on positive gaseous ions as very vigorous oxidants independent of the nature of the gas [1,2,3,4,5]. The principle of the method consists of the following. When current flows in series through a gas and an electrolyte, gaseous ions on which water vapor condenses are obtained in the gas on discharge (compare with process occurring in Wilson chamber). The solvated ions are directed toward the liquid by the electrical field and enter it. In this, if the electron level of positive gaseous ions (hydrogen, helium and oxygen) carried by the electrical field into the sulfite solution is lower than the electron level of the SO_3^{2-} ions existing in solution, then the positive gaseous ions must react with the SO_3^{2-} ions, for example according to the reaction:

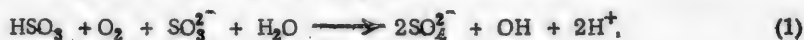


Because of stripping an electron from a SO_3^{2-} ion, it is evident that a product should be formed having a higher degree of oxidation, and thus positive gaseous hydrogen ions, as well as those of other gases, must be oxidants compared to SO_3^{2-} ions.

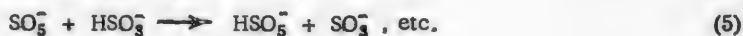
The oxidation of aqueous sodium sulfite solutions has been studied for a long time by many authors from varying viewpoints. This question occupied Titoff [6]. A theory for oxidation of aqueous sodium sulfite solutions was proposed by Haber [7]. Haber's conclusions were based on considerably earlier studies by Baubigny [8,9], who showed that when divalent copper ions were introduced into an aqueous sodium sulfite solution in absence of oxygen, sodium dithionate formed in solution and cuprous oxide deposited as a precipitate. Baubigny gave the following scheme for the course of reaction:



Starting from primary formation of monothionic acid in oxidizing aqueous sodium sulfite solution, Haber gave the following scheme for oxidizing sulfite in presence of oxygen.



Later, Bäckström [10,11] somewhat modified the oxidation scheme proposed by Haber. Bäckström, not denying HSO_3 formation, proposed the following scheme for sulfite oxidation:

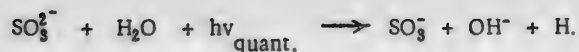


The chain is broken in consequence of the reaction:



The presence of dithionate ions, observed in aqueous sodium sulfite solutions after exposure to light in absence of oxygen, also indicates SO_3 formation, because dithionate ions are formed in this case by combination of monothionate ions into dithionate ions.

Here monothionic acid is formed from sulfite ions because of the action of light in removing an electron, which, in its turn, dissociates a water molecule according to the reaction:



N.A. Shilov [12] appears to be the originator of studies on chain reactions. N.N. Semenov [13] selected in his monograph, as an example of the many types of chain reactions, oxidation of aqueous sodium sulfite solutions, using Haber's theory to explain the process. Later experiments by Gerandes [14] on oxidizing sulfite ions by oxygen led him to deny Haber's theory, since oxidizing sulfite ions with divalent iron ions gave the same effect as did trivalent iron in the Gerandes experiments. According to Gerandes, sulfite oxidation in presence of iron ions takes place on account of oxidation and reduction of iron ions. In absence of oxygen, sulfite oxidizes on account of reducing trivalent iron ions to the divalent form and establishing equilibrium between them.

Generalizing the results of all researchers on oxidizing aqueous sodium sulfite solutions, which are given in the literature, we may conclude that:

a) most workers (Haber, Backström, and others) consider that oxidation of aqueous sodium sulfite solutions, both in presence of catalysts and also by simple photochemical reaction, proceeds via a phase on monothionic acid formation; this is the active center causing reaction;

b) no work was performed using positive gaseous ions as the oxidant.

We studied the reaction of SO_3^{2-} ions, present in aqueous solution, with positive gaseous hydrogen, helium and oxygen ions, directed by an electrical field into an aqueous sodium sulfite solution, in order to explore the processes occurring thereby.

EXPERIMENTAL

1. Electrical equipment. The arrangement of equipment for electrolysis is given in Fig. 1.

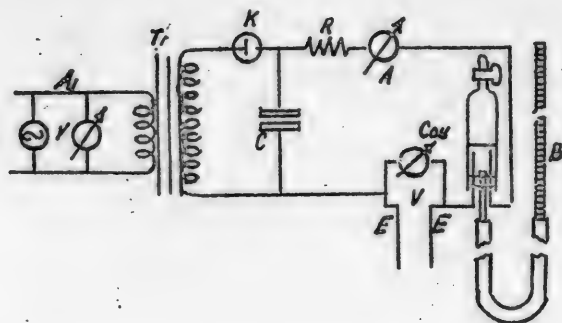


Fig. 1. Arrangement of electrolysis equipment. Tr) transformer for increasing voltage to 2000 - 3000 V; K) kenotron; C) condenser; B) burette; E) electrodes; Cou) Coulometer; A) galvanometer; V) voltmeter; A) lighting circuit.

A direct current having a potential from 2000 to 3000 V was used for electrolysis. The high potential is necessary to obtain discharge through the gas present in the electrolyzer at atmospheric pressure. The latter was provided for the purpose of eliminating the harmful effect of saturated vapors over the solution, i.e., so that there would be a large quantity of the gas molecules of interest (hydrogen, helium, oxygen) in the gas mixture at the moment of discharge. The discharge took place between the end of a platinum electrode 1 mm diameter) and the electrolyte surface in the closed wide leg of the electrolyzer (Fig. 2.).

Electrolyzer construction was developed empirically. The separation between the platinum electrode tip and the electrolyte surface, i.e., the "spark" length, was measured by a cathetometer. Because the gaseous ions produced react on their passage through the electrolyte, the gas volume in the electrolyzer continually decreases, and consequently, the "spark" length changes. The spark

length was held constant during a test by holding a constant electrolyzer solution level, during this, we determined the quantity of gas evolved from or absorbed by the solution during the test period. Measurements were conducted at atmospheric gas pressure both in the electrolyzer and in the aspirator. The second electrode (0.5 mm diameter) was immersed in electrolyte solution which filled the narrow leg of the electrolyzer and was isolated from the air. The quantity of charge passing through the electrolyzer was calculated from the quantity of oxy-hydrogen gas evolved in the coulometer.

Measurements were performed under atmospheric pressure of oxy-hydrogen gas. For the purpose of controlling constancy of the working equipment, an ammeter was included in the secondary circuit and a volt-meter was located in the primary circuit to establish voltage applied to the transformer. The term "spark", used by us above, is not absolutely precise, because a condition of spark discharge in the gas existed in certain circumstances while in others it was one of a high voltage arc.

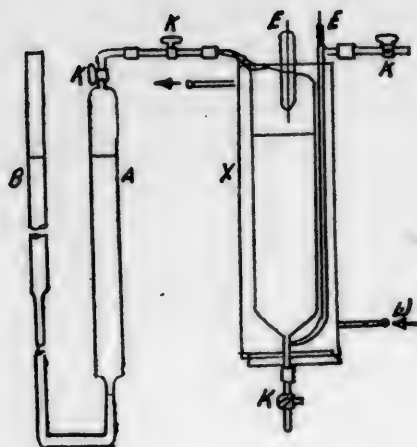


Fig. 2. Electrolyzer arrangement. E) Electrodes; A) gas aspirator; B) but-
rette; K) three-way cock; X) conden-
ser; W) water inlet to condenser.

TABLE 1

Sample No.	Na ₂ SO ₃ concen- tration	Quantity of gas se- parated from solu- (H ₂), or absorbed by solution (O ₂) (ml)	Spark length (mm).
1	1.5 N	194.5	2
2	1.5 N	185.0	2
3	1.5 N	191.0	2
4	1.5 N	238.0	4
5	1.5 N	236.0	4
6	1.5 N	233.0	4
7	0.6 N	111.0	3
8	0.6 N	113.0	3
9	0.6 N	111.0	3
10	1.0 N	167.0	3
11	1.0 N	168.0	3
12	1.0 N	15.0	2
13	1.0 N	14.0	2

In general, all experiments were performed with the elec-
trolyzer shown in Fig. 2, but a portion of the work was per-
formed in an electrolyzer described by V.I. Pavlov [2,3].

2. Experimental Method. In carrying out the experiments
with aqueous sodium sulfite solutions, four fundamental vari-
ables were subjected to measurement: a) change in volume of the gas serving as a source of gaseous ions: b) quan-
tity of electricity passing through the ionizing gas-electrolyte circuit; c) quantity of sulfite ion disappearing from
solution; d) quantity of sulfate ion appearing in solution. In carrying out the experiments, as a rule: a) current
strength passed through electrolyte was 5 mA; b) temperature was that of the room (from 20 to 25°C); c) spark
length was not more than 3 mm or less than 1.5 mm; d) sodium sulfite solution sulfite concentration varied from
0.6 to 1.5 N.

All the stated values were established in practice based on a whole series of supplementary tests. During these
experiments we came upon the fact that certain factors (atmospheric pressure, current strength, spark length, and so
on) did not remain constant during the course even of one experiment. Test temperature variation did not exceed \pm
0.5°. Variation in current strength passing through the electrolyte, did not exceed \pm 0.5 mA. Variation in spark
length during the period of an experiment did not exceed \pm 0.1 mm.

To explore the effect of the stated factors on sulfite solution oxidation rate, we wet up a whole series of supple-
mental experiments. It was necessary to do this because of the complete absence of references to this question in
the literature.

As a result it was shown that experiments performed at the same conditions were reproducible despite slight
inconstancy of certain factors. Discrepancies occurring in experimental results did not usually exceed limits of
experimental accuracy, as can be seen from Table 1.

Note 1. The quantity of electricity passing through the electrolyte was determined by the time in which 10
ml oxy-hydrogen gas was evolved in the coulometer in experiments with O₂, and 5 ml in experiments with H₂.

Note 2. Oxygen was used in experiments 1-11. Hydrogen was used in experiments 12-13.

3. Materials. 1. Chemically pure reagents and acids were used in this work. All sulfite solutions were pre-
served under hydrogen during the entire course of experimentation in order to avoid oxidizing them to sulfate.
The sulfites were analyzed for sulfite and sulfate content, and in some cases for free alkali and also approximate
hydrogen ion concentration (using selected indicators) in the aqueous sodium sulfite solutions.

2. Of the gases used in the experiments, oxygen and helium were obtained commercially but hydrogen
was prepared by action of a caustic soda solution on aluminum turnings followed by a corresponding purification
of the gas. All gases were analyzed for contained impurities using the gasometric system of Knorr, Zimin, and
Platonov.

Hydrogen, as a rule did not contain more than 3% impurity, of which about 0.5% was oxygen. Helium did

not contain oxygen or hydrogen (within the limits of analysis). Oxygen contained about 3.5% nitrogen as an impurity.

DISCUSSION OF RESULTS

I. Explanation of oxidizing tendency of positive gaseous hydrogen, helium, and oxygen ions. For this purpose several series of experiments were performed (Figs. 3 and 4), in which aqueous sodium sulfite solutions were bombarded with gaseous ions—positive, negative, and so on.

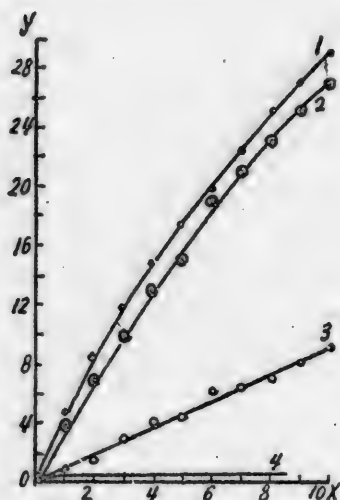


Fig. 3. x) Quantity of oxy-hydrogen gas evolved in coulometer (ml). y) Quantity of H_2 evolved from Na_2SO_3 solution (ml): a) during its bombardment with gaseous hydrogen or helium ions—positive (1 and 2), or negative (3); b) during ordinary hydrolysis (4); c) in experiments with a spark parallel to surface of aqueous Na_2SO_3 solution in electrolyzer (4). 1, 3, and 4) experiments with hydrogen; 2 and 4) experiments with helium.

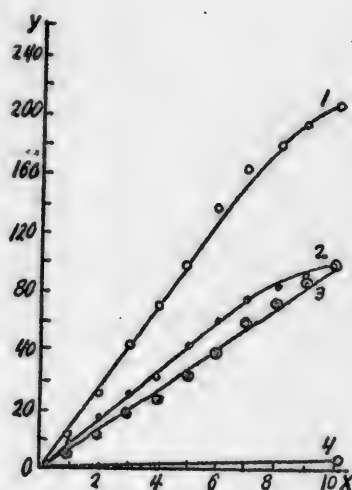


Fig. 4. x) The quantity of oxy-hydrogen gas evolved in coulometer (ml). y) quantity of O_2 absorbed by Na_2SO_3 solution (ml): a) during bombarding solution by gaseous oxygen ions—positive (1), negative (2); b) during ordinary electrolysis (4); c) in experiments with spark parallel to surface of aqueous Na_2SO_3 solution in electrolyzer (3).

It can be seen from the data of Fig. 3 and Fig. 4 that the action of positive gaseous hydrogen, helium, and oxygen ions on a sodium sulfite solution is sharply different from the action of other types of electrolysis and from the action of sparks which are parallel to the sodium sulfite solution surface in the electrolyzer.

The rate of evolving hydrogen from sodium sulfite solution in experiments with positive hydrogen and helium ions and the rate of absorbing oxygen by sodium sulfite solution in experiments with positive oxygen ions was significantly higher than rates in all other series of experiments, and consequently, the rate of sulfite oxidation was also significantly higher. (The relationship between rate of sodium sulfite solution oxidation and the quantity of oxygen absorbed by it or of hydrogen evolved from it during the experiment is given below).

We conclude that positive gaseous hydrogen, helium, and oxygen ions are strong oxidants.

II. Explanation of processes occurring in an aqueous sodium sulfite solution on its bombardment by positive gaseous helium and hydrogen ions.

In the action of positive gaseous hydrogen and helium ions on aqueous sodium sulfite solutions, it was established that: during the period of passing current, continuous hydrogen evolution from solution was observed—gas volume in aspirator continually increased. Independent of the sodium sulfite solution concentration used, the rate of hydrogen evolution from solution remains constant at the beginning of the experiment, and decreases the longer current is passed through the solution (Table 2).

TABLE 2

Experiments with Positive Hydrogen Ions

Oxy-hydrogen gas evolved in coulometer (ml)	Quantity of	
	Hydrogen, evolved by Na ₂ SO ₃ solution (ml) per ml of oxy-hydrogen gas	
	0.6 N Na ₂ SO ₃ solution	1.5 N Na ₂ SO ₃ solution
1	4	4
2	3	3
3	3	3
4	3	3
5	3	2
6	2	4
7	2	2
8	1	2
9	1	2
10	1	2

TABLE 3

Quantity of		SO ₃ ²⁻ ions disappearing from Na ₂ SO ₃ solution		Experi- ment with
Oxy-hydro- gen gas evolved in coulometer (ml)	H ₂ , evolved from Na ₂ SO ₃ solution (ml)	per ml H ₂ evolved	per to- tal H ₂ volume evolved	
3.0	9.0	4.45·10 ¹⁹	4.0·10 ²⁰	H ₂ ⁺
5.8	17.0	4.42·10 ¹⁹	7.51·10 ²⁰	H ₂ ⁺
3.0	8.2	4.68·10 ¹⁹	3.84·10 ²⁰	H ₂ ⁺
5.9	16.3	4.71·10 ¹⁹	7.67·10 ²⁰	H ₂ ⁺
6.0	18.8	3.48·10 ¹⁹	6.55·10 ²⁰	He

TABLE 4

Oxy-hydro- gen gas evolved in coulo- meter (ml)	Quantity of			Experiment with
	SO ₃ ²⁻ ions disappear- ing from Na ₂ SO ₃ so- lution (g BaSO ₄)	SO ₄ ²⁻ ions forming in Na ₂ SO ₃ so- lution (g BaSO ₄)	$\frac{N_{SO_3^{2-}}}{N_{SO_4^{2-}}}$	
3	0.155	0.087	1.78	H ₂ ⁺
5.8	0.294	0.168	1.75	H ₂ ⁺
6	0.254	0.192	1.32	He ⁺

The literature indicates possible formation of hypothetical monothionic acid (HSO₃) which does not exist in the free state (Semenov [13], Rais [15], Haber [7], and others).

According to reaction (12), solution acidity should increase (by 0.007 N according to theoretical calculations). It is necessary, naturally, to note that if a small increase in hydrogen ion concentration takes place in solution, then there must be formed at the same time a corresponding quantity of negative ions. In the case in which there is no vapor in solution (in the form of negative ions) for forming hydrogen ions, then the hydrogen ions give up their charge and are evolved as free hydrogen.

Reduction in rate is explained by change in initial electrolyte composition in consequence of reactions caused by current. During the course of that interval of time during which from 4 to 6 ml oxy-hydrogen gas was evolved in the coulometer the electrolyzer solution remained transparent, and then, with further passage of current through the solution, the latter gradually developed a slight opalescence which increased and turned to a precipitate. The precipitate, as was established analytically, contained sulfur. At the same time that hydrogen was evolved from the sodium sulfite solution, we observed that SO₃²⁻ ions disappeared from solution (Table 3).

The number of SO₃²⁻ ions disappearing from the sodium sulfite solution (Table 3) is proportional to the number of milliliters of hydrogen evolved from the sulfite solution and is also proportional to the quantity of electricity passing through the electrolyte during the experimental period.

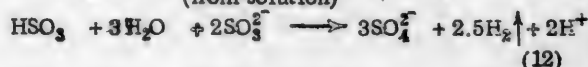
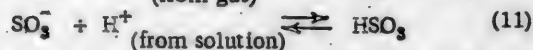
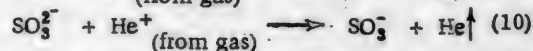
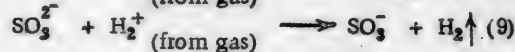
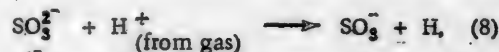
Along with the disappearance of SO₃²⁻ ions from sodium sulfite solution, SO₄²⁻ ions accumulate in solution (Table 4).

N_{SO₃²⁻} is the number of SO₃²⁻ ions disappearing from the Na₂SO₃ solution:

N_{SO₄²⁻} is the number of SO₄²⁻ ions forming in the Na₂SO₃ solution.

The number of SO₄²⁻ ions forming in the sodium sulfite solution is proportional to the number of SO₃²⁻ ions disappearing from solution, but is significantly smaller than the latter (Table 4). This difference is greater with positive hydrogen ions than for helium. These facts may evidently be explained by the following considerations.

In working with positive gaseous hydrogen or helium ions, we may assume that oxidation of aqueous sodium sulfite solutions takes place according to the reactions:



Free hydrogen formation takes place in reactions (8), (9), and (12). Hydrogen at the moment of its evolution is a strong reducing agent, and particularly reduces sulfite. Reduction takes place variously depending on reaction conditions (length of passing current through sodium sulfite solution, sodium sulfite solution concentration, and so on) either to polythionic compounds or to sulfur, as is shown by analyses.

In using positive gaseous helium ions for oxidation of aqueous sodium sulfite solutions, fewer side reactions can take place, because on neutralizing the positive helium ions (reaction 10), the inert gas evolved does not react with any of the ions present in solution.

Sulfite reduction is possible in this case only on account of hydrogen evolved by reaction 12 or on account of usual cathodic reduction, as also takes place when working with positive hydrogen ions.

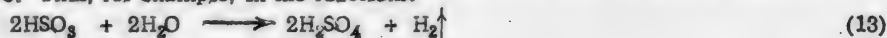
In working with helium, this evidently also explains the smaller loss of SO_3^{2-} ions from sodium sulfite solution during formation of the same amount of SO_4^{2-} ions by passing the same quantity of electricity through the solution and on evolving the same number of milliliters of hydrogen from solution as in experiments with hydrogen.

According to reaction (12), per unit elementary charge introduced from the gas, three SO_4^{2-} ions should be formed in solution, and 2.5 molecules of hydrogen should be evolved from solution.

It was shown experimentally, that per elemental charge introduced from the gas into a 1.0 N concentration sulfite solution, 2.7 SO_4^{2-} ions were formed and from 2.2 to 2.5 molecules of hydrogen were evolved in the experiments with hydrogen; in the experiments with helium: 2.75 SO_4^{2-} ions and 2.2-2.9 molecules of hydrogen.

These data closely approach equation (12) despite its complexity in view of the large number of molecules taking part in the reaction.

Our attempts to find a simpler reaction scheme for oxidizing sodium sulfite by positive gaseous hydrogen and helium ions was not effective. Thus, for example, in the reactions:



or



the quantity of SO_4^{2-} ions formed in solution and the quantity of free hydrogen evolved, calculated according to equations (13) and (14) do not agree with data obtained experimentally.

III. Explanation of processes taking place in an aqueous sodium sulfite solution during its bombardment with positive gaseous oxygen ions. In action of positive gaseous oxygen ions on an aqueous sodium sulfite solution, it was established that during the period of current passage, continuous oxygen absorption by the solution was observed, such that the aspirator gas volume continually decreased.

Independent of the sodium sulfite solution concentration employed, the rate of oxygen absorption by the solution, which remained more or less constant at the start of the test, decreased with increasing passage of current through the solution (Table 5).

TABLE 5

Oxy-hydrogen gas evolved in coulometer (ml)	Quantity of		
	Oxygen (ml) absorbed by Na_2SO_3 solution per ml oxy-hydrogen gas		
	1.3 N Na_2SO_3 solution	1.0 N Na_2SO_3 solution	1.5 N Na_2SO_3 solution
1	25	19	25
2	25	17	23
3	25	18	20
4	24	17	21
5	29	20	23
6	22	18	19
7	27	17	17
8	24	13	17
9	21	14	17
10	13	14	13

The reduction in rate is explained by change in initial electrolyte composition in consequence of reactions caused by the current. The quantity of oxygen absorbed by the sodium sulfite solution at the start of the experiment is proportional to the quantity of electricity passing through the electrolyte. Preservation of this proportionality depends on many factors (spark length, and so on). Simultaneously with oxygen adsorption by sodium sulfite solution, a disappearance of SO_3^{2-} ions from solution was observed (Table 6):

$N_{\text{SO}_3^{2-}}$ is the number of SO_3^{2-} ions disappearing from the Na_2SO_3 solution; N_{O_2} is the number of oxygen molecules adsorbed by the Na_2SO_3 solution.

Along with the disappearance of SO_3^{2-} ions from sodium sulfite solution, SO_4^{2-} ions accumulate in

TABLE 6

O ₂ absorbed by Na ₂ SO ₃ solution (ml)	NO ₂	Quantity of SO ₃ ²⁻ ions disappearing from Na ₂ SO ₃ solution		N _{SO₃²⁻} NO ₂
		Per ml oxygen absorbed	Per total volume of oxygen absorbed	
148	3.97·10 ²¹	5.30·10 ¹⁹	7.34·10 ²¹	1.98
173	4.65·10 ²¹	5.37·10 ¹⁹	9.3·10 ²¹	2.00
225	6.03·10 ²¹	5.16·10 ¹⁹	11.6·10 ²¹	1.92
351	9.43·10 ²¹	5.26·10 ¹⁹	18.4·10 ²¹	1.95

solution (Table 7).

N_{SO₄²⁻} is the number of SO₄²⁻ ions forming in Na₂SO₄ solution.

It can be seen from Tables 6 and 7:

$$(1) \frac{N_{SO_3^{2-}}}{N_{O_2}} \approx 2; \quad (2) \frac{N_{SO_3^{2-}}}{N_{SO_4^{2-}}} \approx 1.$$

From which we obtain:

$$(3) \frac{N_{SO_4^{2-}}}{N_{O_2}} \approx 2.$$

Consequently, the overall process of oxidizing a sodium sulfite solution by positive gaseous oxygen ions takes place according to the reaction:



Naturally, depending on experimental conditions, NO₂ appearing per unit elementary charge introduced from the gas is different (Table 8).

Per unit elementary charge introduced from the gas, in working with positive gaseous oxygen ions, from 1.5 to 20 molecules of oxygen are absorbed (Table 8), and consequently, from 3 to 40 ions of SO₄²⁻ are formed (Formula 3), i.e., the process of sulfite oxidation takes place here as a chain reaction.

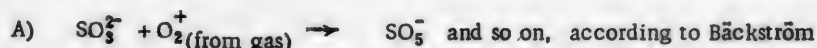
Based on the experiments performed, we should regard the oxidation of aqueous sodium sulfite solutions by positive gaseous oxygen ions as the result of several processes:

1) Simple oxygen absorption by aqueous sodium sulfite solution. This process takes place slowly and has almost no effect on the experimental results.

2) Absorption in solution of activated oxygen which forms in the discharge (ozone or atomic oxygen). Formation of activated oxygen in the spark was confirmed both in the experiments with sparks parallel to the solution surface in the electrolyzer and in experiments with negative oxygen ions (Fig. 4.)

3) Direct oxidation of SO₃²⁻ ions by positive gaseous oxygen ions as a result of exchanging their charge with the SO₃²⁻ ions.

For example, according to the reactions:



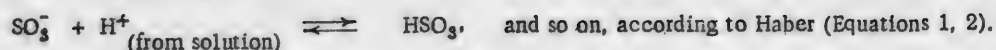
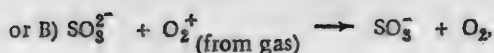
(Equations 5, 6)

TABLE 7

SO ₃ ²⁻ ions disappearing from Na ₂ SO ₃ solution	Quantity of SO ₄ ²⁻ ions forming in sulfite solution		N _{SO₃²⁻} N _{SO₄²⁻}
	g BaSO ₄	N _{SO₃²⁻}	
0.637	1.64·10 ²¹	0.600	1.55·10 ²¹
0.628	1.78·10 ²¹	0.692	1.79·10 ²¹
0.728	1.87·10 ²¹	0.677	1.75·10 ²¹
0.784	2.02·10 ²¹	0.760	1.96·10 ²¹

TABLE 8

Na ₂ SO ₃ solution concentration	Quantity of oxygen evolved in coulometer (ml)	NO ₂ per unit elementary charge, introduced from gas	Spark length (mm)
1.5 N {	0-3	17	2
	4-6	16	
1.5 N {	0-3	18	4
	4-6	16	
1.5 N {	0-3	21	1.7
	4-6	18	
1 N {	0-3	10	1.7
	4-6	11	
0.6 N {	0-3	6	1.7
	4-6	6	
0.1 {	0-3	1.5	1.7
	4-6	1.5	



4) Combination with oxygen, according to reaction (15), formed from positive gaseous ions after discharging their charge.

The overall process of oxidizing aqueous sodium sulfite solutions, despite the various intermediate reactions, corresponds to reaction (15).

SUMMARY

1. Electrolyzer construction and method of operation were developed.
2. It was shown that the action of positive gaseous hydrogen, helium, and oxygen ions on a sodium sulfite solution is sharply different from the action of other types of electrolysis and from the action of sparks parallel to the Na_2SO_3 solution surface in the electrolyzer.
3. A reaction scheme was proposed according to which positive gaseous hydrogen and helium ions oxidize an aqueous sodium sulfite solution.
4. It was shown that the purest oxidation condition was observed on using positive helium ions as the oxidant, because positive hydrogen ions partially reduce sulfite ions after their neutralization.
5. It was explained that oxidation of aqueous sodium sulfite solutions by positive gaseous oxygen ions takes place as a chain reaction, and the final oxidation result corresponds to the reaction:

$$2\text{Na}_2\text{SO}_3 + \text{O}_2 = 2\text{Na}_2\text{SO}_4$$
6. It was shown that positive gaseous hydrogen, helium and oxygen ions are extremely strong oxidants.
7. The method of oxidation by positive gaseous ions is significantly stronger than the method of ordinary electrolysis, and is particularly pure in case inert gases are used.

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Received April 25, 1953

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REDUCTION OF SILICOTUNGSTATES BY HYDROGEN

VI. METHODS OF ANALYZING SILICOTUNGSTATES AND TUNGSTEN BRONZES

E. A. Nikitina and A. S. Kokurina

In our previously published four contributions [1,2,3,4] methods were given for preparing and for carrying out numerous analyses on various potassium silicotungstates and tungsten bronzes. The present paper is devoted to a description of those methods of analysis which were used to establish compositions of silicotungstates, bronzes, and products of their reduction by hydrogen.

Analysis of silicotungstic acid and its salts consisted in determining water, SiO_2 , WO_3 , K_2O (or Na_2O), and Cl^- . Determination of water was by the usual method — drying and ignition to constant weight. The end of ignition was determined by color change in the sample, which acquired a greenish-yellow color of WO_3 .

Determination of K_2O . A sample of about 1 g of the substance was dissolved in water and precipitated with quinoline acetate. The precipitant was prepared from 2 ml quinoline, 2 ml concentrated acetic acid, and 100 ml water. After thoroughly washing twice with diluted precipitant, the quinoline silicotungstate precipitate was taken for subsequent SiO_2 and WO_3 determination. The filtrate and wash waters were evaporated; the dry residue gently calcined, converted to K_2SC_4 by addition of H_2SO_4 , and finally weighed in the form of this compound.

Determination of SiO_2 and WO_3 . The quinoline silicotungstate precipitate was dried in an oven at 80° , and heated and ignited in a porcelain crucible to constant weight.

The SiO_2 and WO_3 oxides obtained were transferred to a platinum or quartz boat and treated with hydrogen chloride in a tube furnace at 600° ; WO_3 vaporized as the basic chloride, WCl_5 ; SiO_2 remained in the boat and was weighed. It is expedient to check the SiO_2 for purity by evaporation with $\text{HF} + \text{H}_2\text{SO}_4$; WO_3 is determined by difference.

Quinoline silicotungstate is water-insoluble, and consequently, it is very convenient to use it for precipitating heteropolar anions; in some experiments, the complex was precipitated with cinchonine, which also gives an insoluble compound with silicotungstate anions.

In a number of experiments with samples having low K_2O content, the silicotungstate analyses were conducted by another method: the sample of ignited salt following water determination was treated with hydrogen chloride at a 600° temperature; hydrogen chloride volatilizes WO_3 ; the residue was dissolved in water and filtered from the SiO_2 ; KCl in the filtrate was titrated by AgNO_3 (Mohr method), and SiO_2 was checked for purity by vaporization with $\text{HF} + \text{H}_2\text{SO}_4$.

In several experiments, a colorimetric method was used for determining SiO_2 quantity based on forming silicomolybdic anions as a result of reaction between SiO_3^{2-} and ammonium paramolybdate. For this a 0.5 g sample of the substance being analyzed was melted in a platinum crucible with 0.3 g sodium acetate. The melt obtained was extracted with 30–40 ml water in a 100–150 ml beaker; the solution was filtered into a 50 ml volumetric flask, brought to the mark and thoroughly mixed. 5–10 ml of the prepared solution was pipetted from the flask and titrated with 2 N HCl to methyl orange; in this manner we established the quantity of HCl necessary to bring the medium to a definite pH in the subsequent colorimetry. Subsequently, a similar 5–10 ml portion of the test solution was taken with a pipette into a tube having dimensions 20 x 2, the quantity of 2 N HCl already established as necessary was added with 0.2 ml excess and thoroughly mixed. After this, 3 ml ammonium molybdate solution was added, the mixture mixed, and the tube set in a steam bath for 5 minutes at $60\text{--}70^\circ$. After gradual cooling, the solution was poured from the tube into a graduated cylinder or an Egerts tube and colorimetrically against a standard solution prepared separately.

Chlorine determination was conducted by an iodometric method developed by Zvenigorodskaya and Gotsdiner [5].

Determination of saponifiable and unsaponifiable alkali in silicotungstate samples which were reduced by hydrogen. A sample weighing 5 to 15 g was wrapped in a packet of dense filter medium and treated in a Soxhlet apparatus

with hot water for a period of 5-6 hours. After this treatment, the solution containing SiO_2 , WO_3 , and K_2O was evaporated to dryness and dried in a drying oven at 130-150° (for a period of 3-4 hours) to remove free HCl. The dry residue was treated with hot water and filtered. A residue containing H_2WO_4 and SiO_2 remained on the filter and KCl was found in the filtrate.

The residue was heated in a platinum crucible and then treated with a few drops of H_2SO_4 (density 1.84) and dried on a water bath. The ignited residue of $\text{WO}_3 + \text{SiO}_2$ was treated with hydrogen chloride and weighed. SiO_2 was checked for purity by vaporization with $\text{H}_2\text{SO}_4 + \text{HF}$, and WO_3 determined by difference. The filtrate, containing HCl, was titrated using 1/20 N AgNO_3 (Mohr method).

Determination of oxygen in silicotungstates. A 1g sample of the substance after water determination was placed in a molybdenum boat and reduced in an electric furnace at a temperature of 800° for a 2.5 hour period (to constant weight) in a dry pure electrolytic hydrogen atmosphere. Oxygen was determined by weight loss.

Analysis of Bronze for Its $\text{K}_2\text{O}(\text{Na}_2\text{O})$ and Tungsten Content

A sample of the substance weighing about 1 g was calcined in a muffle at a 550-600° temperature to constant weight; the tetravalent tungsten of the tungsten bronze was converted to W^{6+} . After calcination, the sample is subjected to hydrogen chloride treatment; as a result of hydrogen chloride action tungsten is quantitatively vaporized as WCl_6 ; the residue from hydrogen chloride treatment contains potassium (sodium) as chloride, which is titrated using silver nitrate (Mohr method).

In conclusion, we note that methods for analyzing tungsten bronzes for sodium were fully given in the work of V.I. Spitsyn [6]. In 1950, Arne Magneli [7] proposed the following method for analyzing tungsten bronze; WO_3 is vaporized by heating at a temperature of 500° in a stream of hydrogen chloride and oxygen; the bronze forms a residue of sodium chloride. Following solution in water, the quantity of chloride is determined by titration with silver nitrate (by Mohr method). In another variant of the method of analysis, the bronze is decomposed by heating with ammonium persulfate. After treatment by water, the ammonium salt is oxidized with aqua regia; sulfuric acid is removed by heating and evaporating to dryness. Alkali metal ions are isolated on an ion exchanger, regenerated with hydrochloric acid, and determined by argentometry; tungsten is precipitated as its mercuric oxide salt; the oxygen content is determined by decomposing the bronze using an alkaline $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution and determining its excess iodometrically.

A. Magneli notes that the method proposed by him is not suitable for analyzing tetragonal sodium bronze. As can be seen from the presented description, this foreign method has more limited applicability and is significantly more complicated than the methods which we use in the present paper.

SUMMARY

1. A method for analyzing silicotungstic acid and its salts is described, which consisted in determining water, SiO_2 , WO_3 , K_2O , Na_2O , and Cl^- .
2. A method is proposed for determining saponifiable and unsaponifiable alkali in hydrogen-reduced silicotungstate samples.
3. A method is given for determining oxygen in silicotungstates as well as a method for analyzing bronze for its K_2O and tungsten content.

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STUDY OF COMPLEX FORMATION IN TERNARY SYSTEM SOLUTIONS

BY METHODS OF PHYSICO-CHEMICAL ANALYSIS.

V. THE SYSTEM: SbBr_3 - AlBr_3 - $\text{C}_6\text{H}_5\text{Cl}$

E. Ya. Gorenbein

In studying the SbBr_3 - AlBr_3 - $\text{C}_6\text{H}_5\text{Cl}$ system [1] by the electrical conductivity method, it was shown that the binary systems SbBr_3 - $\text{C}_6\text{H}_5\text{Cl}$ and AlBr_3 - $\text{C}_6\text{H}_5\text{Cl}$ conduct almost no current. However, the ternary system SbBr_3 - AlBr_3 - $\text{C}_6\text{H}_5\text{Cl}$ is a current conductor. The appearance of conductivity in systems consisting of components which do not conduct current in their individual liquid states is explained by the formation of current conducting complexes.

Investigation of this system was performed in such a way that the molecular ratio between aluminum bromide and chlorobenzene remained constant, changing the concentration of antimony bromide. However, we were not able to establish the composition of the compound formed in solution despite the fact that the molecular ratio of SbBr_3 to AlBr_3 somewhat exceeded an equimolar mixture of these components.

Thus, for a molecular ratio of AlBr_3 to $\text{C}_6\text{H}_5\text{Cl}$ equal to 0.102, the molecular ratio of SbBr_3 to AlBr_3 attained 2.387; with a molecular ratio of AlBr_3 to $\text{C}_6\text{H}_5\text{Cl}$ of 0.23, the molecular ratio of SbBr_3 to AlBr_3 attained 1.874; and with molecular ratios of AlBr_3 to $\text{C}_6\text{H}_5\text{Cl}$ equal to 0.35-0.36, the highest molecular concentration ratio of SbBr_3 to AlBr_3 reached 1.39, and even on the specific electrical conductivity-composition curves there were none of the special characteristic cusps by which one could judge the composition at which a complex formed in solution.

Naturally, it was of interest to study this system using a modified method for changing the concentration of system components in such a manner that one component, used as a solvent, should remain constant, and that concentrations of the remaining two should change according to such a rule that the sum of their gram-molecules should remain constant.

EXPERIMENTAL

Initial materials and method of working. Aluminum bromide and antimony bromide were prepared and stored in the very manner which was described in our previous paper [2]. Chlorobenzene after careful purification was dried over fused calcium chloride and distilled into an elongated tube which was immediately sealed when filled. In this work we used a preparation distilling at constant temperature. Solutions of appropriate concentration were prepared in a conical flask with side-tube. The calculated quantity of chlorobenzene was added from a burette to the AlBr_3 - SbBr_3 melt. The $\text{C}_6\text{H}_5\text{Cl}$ quantity added was checked by weighing. To preserve the solutions from traces of moisture, the burette (25 ml) communicated with the air through a calcium chloride tube filled with drying agent.

After filling the vessels for electrical conductivity, viscosity and pycnometry with the solutions, the tubes were placed in a water thermostat and were taken for test after passage of some time. Variation of thermostat temperature did not exceed $\pm 0.1^\circ$.

Electrical conductivity was measured using a lamp generator and optical indicator [3].

Electrical conductivity, viscosity, and density. The SbBr_3 - AlBr_3 system was studied in the liquid state for fusibility [4], electrical conductivity [5, 6], and viscosity [6] over the full range of concentrations. According to these data, the electrolyte is a complex having the composition $\text{SbBr}_3 \cdot \text{AlBr}_3$.

Electrical conductivity of this same system was studied in a variety of organic solvents (benzene, toluene, nitrobenzene, ethylene bromide, and so on) which form compounds with components present in the given complex. Chlorobenzene does not form a compound either with SbBr_3 [7] or with AlBr_3 separately. This significantly eases solving the question on electrolyte composition in solution and together with this makes possible explanation of the

than the $\text{SbBr}_3 + \text{AlBr}_3$ concentration, which we knew. Thus the coefficients were equal to: $a = 1.930 \cdot 10^{-2}$ and $\beta = 4.143 \cdot 10^{-2}$, where the temperature coefficient was calculated for the temperature interval from 15 to 20° for the 0.2 isomolar concentration, and where the concentration coefficient was calculated for a temperature of 20° and for a range of isomolar concentrations from 0.2 to 0.3. We expect that further study will make it possible to establish interrelations between these coefficients.

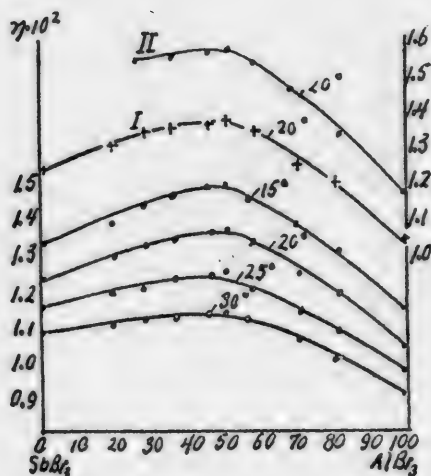


Fig. 1. Dependence of $\text{SbBr}_3 - \text{AlBr}_3 - \text{C}_6\text{H}_5\text{Cl}$ system viscosity on ratio of antimony bromide to aluminum bromide. (I) 0.2 Isoconcentration; (II) 0.3 isoconcentration.

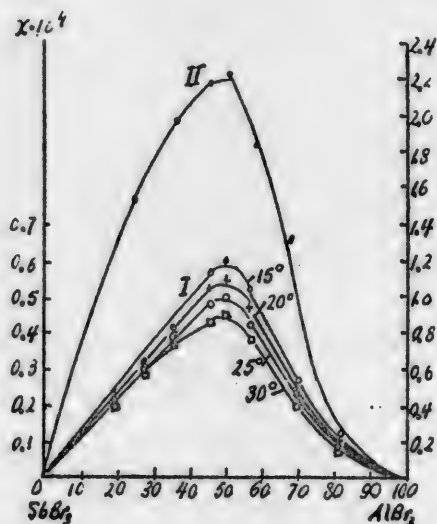


Fig. 2. Dependence of specific electrical conductivity on antimony bromide : aluminum bromide concentration ratio at 20° . (I) 0.2 Isoconcentration; (II) 0.3 isoconcentration at 20°

The Fig. 2 curves give the dependence of specific electrical conductivity on ratio of antimony bromide concentration to that of aluminum bromide. The conductivity maximum indicates the composition of the electrolyte forming in solution. As with the viscosity data, so also for electrical conductivity—the complex composition in solution is expressed by the formula: $\text{SbBr}_3 \cdot \text{AlBr}_3$.

The curves marked with a Roman numeral I were constructed from data at an isomolar concentration of 0.2, while the curves marked with a Roman numeral II are for isomolar concentrations equal to 0.3. The numbers on the right hand ordinate axis refer to curves II.

The effect of temperature and concentration on system conductivity is shown in Fig. 2. With increase in temperature, the specific electrical conductivity decreases somewhat (curves I). This, evidently, is explained by decomposition of the current-conducting complex into its constituent components. Increase in concentration, i.e., transition to a higher isomolar concentration for the $\text{SbBr}_3 + \text{AlBr}_3$ components leads to a significant increase in solution conductivity. This is connected with significant increase in degree of association of the electrolyte forming in solution.

As is known, in solvents with a small D_n , with increase in electrolyte concentration, its degree of association increases; together with this, the solution electrical conductivity increases. Thus, for example, increase in concentration of the $\text{SbBr}_3 \cdot \text{AlBr}_3$ complex in aluminum bromide as a solvent leads to an increase in its molecular weight; at a concentration of 2.76% the molecular weight is 668, and at 22.52% it is equal to 1850 [9]; along with this, the electrical conductivity also increases [5, 6]. Conductivity of this complex in a benzene solution, at concentrations at which its molecular weight is equal to its formula weight according to cryoscopic data, is very small. Thus, with a 15% concentration of complex in benzene, its molecular weight is close to its formula weight and its electrical conductivity is equal to $0.8 \cdot 10^{-7}$ mho [10]. With increase in concentration, molecular weight increases and so does solution conductivity. This is in complete agreement with the law for reducing corrected molar electrical conductivity in diluting high concentration solutions [11].

effects of dilution and temperature on system viscosity changes. For this purpose, we studied electrical conductivity, viscosity, and density of the stated system at two isomolar concentrations, equal to 0.2 and 0.3, and at 15, 20, 25, and 30°.

Results of measurements at a 20° temperature are given in Tables 1 and 2; the other data are given graphically.

TABLE 1

Molecular ratio $\frac{\text{SbBr}_3 + \text{AlBr}_3}{\text{C}_6\text{H}_5\text{Cl}} = 0.2$
Temperature 20°

$\frac{\text{SbBr}_3 + \text{AlBr}_3}{\text{C}_6\text{H}_5\text{Cl}}$ (Moles)	Mol. % AlBr ₃	d_{40}^t	$\eta \cdot 10^2$	$\kappa \cdot 10^4$
0.1989	100	1.3749	1.034	—
0.2003	81.05	1.4092	1.180	0.110
0.2004	70.31	1.4288	1.241	0.252
0.1999	57.37	1.4506	1.333	0.474
0.1998	50.58	1.4628	1.361	0.549
0.2006	46.15	1.4704	1.352	0.524
0.2004	36.15	1.4886	1.342	0.409
0.200	28.88	1.4989	1.329	0.312
0.1995	19.19	1.5088	1.299	0.233
0.1992	0	1.536*	1.226*	—

TABLE 2

Molecular ratio $\frac{\text{SbBr}_3 + \text{AlBr}_3}{\text{C}_6\text{H}_5\text{Cl}} = 0.3$

$\frac{\text{SbBr}_3 + \text{AlBr}_3}{\text{C}_6\text{H}_5\text{Cl}}$ (Moles)	Mol. % AlBr ₃	d_4^t	$\eta \cdot 10^2$	$\kappa \cdot 10^4$
0.2999	100	1.4811	1.159	—
0.2977	81.78	1.5271	1.319	0.259
0.2994	68.08	1.5621	1.449	1.129
0.3000	58.90	1.5838	1.526	1.843
0.3005	51.51	1.6041	1.558	2.223
0.3008	46.41	1.6136	1.548	2.181
0.2969	36.50	1.6303	1.541	1.976
0.3011	25.77	1.6631	1.536	1.553

Variation of system viscosity with ratio of components (SbBr₃ to AlBr₃) for the two isomolar

concentrations 0.2 and 0.3, during which the total number of gram molecules of these components was taken as 100 mol.%, is shown in Fig. 1. Isothermal curves for 15, 20, 25, and 30° characterize the variation in system viscosity for an isomolar concentration equal to 0.2.

For a graphical presentation we compare two curves in this figure: I— for an isoconcentration equal to 0.2 at a 20° temperature, and II— for the very same temperature at an isoconcentration of 0.3. The scale on the right-hand ordinate axis remains the same, but numerical values have been shifted upward somewhat for convenience. It can be clearly seen from the data presented that decreasing concentration or increasing temperature leads to reducing system viscosity, although naturally to varying degrees.

If one compares SbBr₃—AlBr₃ system viscosity in the molten state [6] with our data for the ternary system, then it is completely clear that addition of an indifferent solvent gradually reduces system viscosity, i.e., the largest viscosity will be observed at that time when the complex forming in the system appears in the pure liquid state under otherwise equal conditions. Such a picture was observed by N. Kurnakov and I. Kvyat [8] in their study of the aniline-mustard oil-toluene ternary system. This kind of study should furnish material for theoretical calculations of the effect of an indifferent solvent or temperature on system viscosity, if either its dependence on temperature is known or if the dependence of system viscosity on indifferent solvent added is known.

Since the viscosity curve maxima correspond to an equimolar composition for the compound forming in solution, we calculated the temperature and concentration viscosity coefficients for this electrolyte according to the formulas:

$$\alpha = \frac{\eta_{t_2} - \eta_{t_1}}{\frac{\eta_{t_2} + \eta_{t_1}}{2} \cdot (t_2 - t_1)};$$

$$\beta = \frac{\eta_{c_1} - \eta_{c_2}}{\frac{\eta_{c_1} + \eta_{c_2}}{2} \cdot \left(\frac{1}{C_1} - \frac{1}{C_2} \right)}.$$

For our isomolar concentrations of 0.2 and 0.3, in consequence of reaction between the components SbBr₃ and AlBr₃ to form a complex having the composition SbBr₃·AlBr₃, concentration of the latter was smaller by 2-fold

* The numbers marked with asterisks were obtained by extrapolating data for the SbBr₃—C₆H₅Cl binary system measured at temperatures of 35, 40, and 45°; (at lower temperatures crystalline SbBr₃ separates).

In conformity with this law, the highest system electrical conductivity would correspond to the corrected electrical conductivity of the individual liquid electrolyte. This state corresponds to the highest degree of association [9]. Depending on the amount of dilution, the degree of association decreases, electrical conductivity falls, and the electrical conductivity maximum becomes more sloped; at a molecular electrolyte state corresponding to the molecular weight $\text{SbBr}_3 \cdot \text{AlBr}_3$, in solvents with small D_n , the conductivity is smallest. The maximum is almost levelled off. In solvents with large D_n , this point corresponds to a minimum molecular electrical conductivity. Further dilution of these solvents leads to electrolytic dissociation of the neutral ion pairs according to the laws of dilute solutions and the molecular weight here will already be less than the formula weight.

A consequence resulting from the laws of high concentration electrolytic solutions to the effect that the electrolyte in solution should be observed at its lowest conductivity in the monomolecular state, was confirmed by us for other electrolytes in various solvents.

SUMMARY

1. Viscosity, electrical conductivity, and density of the $\text{SbBr}_3\text{--AlBr}_3\text{--C}_6\text{H}_5\text{Cl}$ system were studied over the entire range of SbBr_3 and AlBr_3 concentrations, at two isomolar concentrations and at varying temperatures.

2. It was shown that the use of our method for studying ternary systems gives more satisfactory data for judging the composition of complex compounds forming in solution.

3. It was established that the reason for appearance of conductivity in this system was the formation of a complex compound having the composition $\text{SbBr}_3 \cdot \text{AlBr}_3$.

4. It was shown that maximum conductivity was reduced on transition from a higher isoconcentration to a lower one, and that reduction in degree of association of the electrolyte was in full agreement with the law for decrease in corrected molecular electrical conductivity of high concentration electrolyte solutions on dilution.

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Received March 7, 1953

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VAPOR-LIQUID PHASE EQUILIBRIA IN THE $P_2O_5-H_2O$ SYSTEM

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A mixture is formed on thermal degradation of orthophosphoric acid, or by its reaction with phosphoric anhydride, which contains various phosphoric acids: orthophosphoric, H_3PO_4 ; pyrophosphoric, $H_4P_2O_7$; triphosphoric acids: orthophosphoric- $H_5P_3O_{10}$; and metaphosphoric acids having the general formula $(HPO_3)_n$. We will call such a mixture "strong phosphoric acid".

Mutual transformations of the stated acids, except for polymerized metaphosphoric acids, take place rather rapidly; consequently, the ratio of acids in the mixture is determined by the total phosphoric anhydride content and does not depend on the method by which the mixture was prepared [1, 2, 3], if formation of polymerized metaphosphoric acids is excluded. From this it follows that vapor pressure in the $P_2O_5-H_2O$ system is uniquely determined by the liquid phase phosphoric anhydride content (with the above stated reservation).

Data published in the literature on variation of vapor pressure over phosphoric acids with temperature and composition [4-8] covers a wide range of phosphoric anhydride content. However, these data are limited - up to a pressure of only one atmosphere. Results of measuring vapor pressure over phosphoric acids at pressures of one atmosphere and higher are presented below.

Method of Measurement

Measurements were performed in an apparatus (Fig. 1), a novel feature of which was use of the liquid whose vapor pressure was being determined as a manometric fluid in a differential manometer. A U-shaped tube was used for this; its narrow arm was closed and filled with liquid at the start. Liquid level in the open arm was thus lower than its level in the closed arm (in selecting the difference in levels it is necessary to consider liquid expansion on heating). Inert gas pressure, measured with a manometer, was maintained over the liquid in the open arm. Subsequently, the U-tube was gradually heated. At some particular temperature a bubble of vapor is formed in the closed arm. At this moment, saturated vapor presses on the liquid in the closed arm and inert gas presses on the liquid in the open arm. On further increase in temperature, the liquid level in the closed arm decreases with a simultaneous rise in level in the open one. The levels are equal at equilibrium between the saturated vapor pressure and the inert gas pressure. The manometer reading directly gives the liquid vapor pressure corresponding to the temperature at which the levels are equal. For increasing measurement accuracy, one should proceed slowly close to this temperature. Since the vapor phase volume is small, its formation does not involve significant change in liquid composition. Measurements at atmospheric pressure were conducted in a pyrex glass tube; here air was used as the inert gas. Heating was provided by an air thermostat or by a bath containing a molten mixture of KNO_3 and $NaNO_2$. The moment the levels were equal was fixed by direct observation.

Our tests of a number of materials showed that copper was significantly more resistant to the action of strong phosphoric acid at high temperatures than various grades of steel, bronze, brass, and other alloys. Consequently, a tube prepared from a red copper ore (cuprite), was used for measurements at pressures above atmospheric. A molten mixture of KNO_3 and $NaNO_2$ was used for heating. The differential manometer null position in this case was determined by closing a contact employing the rather high electrical conductivity of phosphoric acid.

Apparatus construction is shown in Fig. 1. The copper U-tube 1, filled with phosphoric acid of known composition, was connected to manifold 2, on which were mounted two fine-regulating small gas valves 3, 4, a precision manometer 5 (one scale division was equal to 0.1 atm), a water cooling coil 6, and an airplane engine spark plug

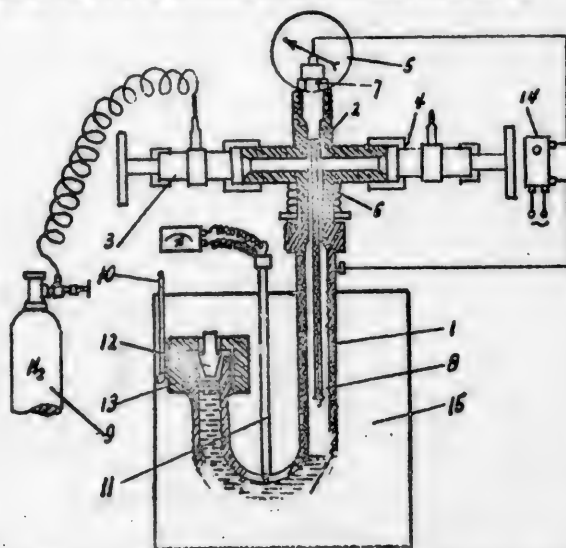


Fig. 1. Equipment arrangement for determining vapor pressures over phosphoric acids at pressures greater than 1 atm. Explanation (of symbols) is given in text.

used for introducing electrode 7. A copper wire, insulated by a porcelain sleeve along its entire length, served as electrode 8 and was soldered to the spark plug. The bare end of the wire was placed at the zero level. The moment contact was made by the acid touching the bare electrode end was indicated by the signal lamp of electronic relay 14. The apparatus is connected to a compressed nitrogen cylinder 9 by valve 3. Valve 4 is used for regulating pressure. Temperature is measured by thermometer 10 immersed in bath 15 and by thermocouple 11 mounted on the measuring tube. For convenience in filling the measuring tube with acid, the seal on the short arm was made using a conical plug 12 and union-nut 13. To establish the necessary difference in levels, excess acid was removed from the open arm by connecting the tube to an evacuated tube via a glass capillary set at the zero level.

Strong phosphoric acid was prepared by heating crystalline orthophosphoric acid (analytically pure) with previously distilled phosphorous pentoxide in a pyrex glass flask at 180° for a 8-50 hour period until the solution was completely homogeneous. Samples were analyzed for total phosphoric anhydride by a gravimetric procedure - precipitation of phosphoric anhydride using ammonium molybdate [9], by a method of potentiometric titration with quinhydrone and calomel electrodes [10], and by directly titrating a sample of acid being analyzed after first boiling it in water - using thymolphthalein.

The difference between results determined by the several methods did not exceed 0.5% P_2O_5 . The samples prepared contained from 29 to 80 weight% phosphoric anhydride.

Results of Measurement

The first series of measurements involved determining the temperature at which the vapor pressure over phosphoric acid was equal to 1 atm. The low volatility of phosphoric acid enables assuming that the gas phase over it consists almost entirely of water vapor up to temperatures of 350-380°. According to Brown and Whitt [8], the gas phase over phosphoric acid contains 0.47 wt. % P_2O_5 at 300° and 1.96 wt % P_2O_5 at 385°. On this basis, we may assume that the values obtained by us for vapor pressures over phosphoric acids correspond to the water vapor pressure. Measurement results are given in Table 1 and illustrated graphically in Fig. 2.

It should be particularly noted that a singular point is present on the composition-temperature isobar (Fig. 2.) which corresponds to transition from aqueous orthophosphoric acid solutions to strong phosphoric acid. Phosphoric anhydride content at this point corresponds to the formula H_3PO_4 . This fact was not noted in any of the earlier papers on determining vapor pressures in the P_2O_5 - H_2O System.

In Fig. 2 we compare literature data on dependence of phosphoric acid composition on temperature at constant vapor pressure with results from the present study. The data of the several authors agree very well for orthophosphoric acid solutions. Our data are somewhat different from literature values for strong phosphoric acid; this, evidently, is explained by the difference in methods used in performing the measurements.

The curve given in Fig. 2 may be used for determining phosphoric anhydride content of phosphoric acids. For this it is necessary to determine the temperature at which test sample vapor pressure becomes equal to atmospheric pressure.

TABLE 1

Dependence on Liquid Phase Composition of Temperature at which Vapor Pressure was 1 atm in P_2O_5 - H_2O System.

Wt. % P_2O_5	Temperature	Wt. % P_2O_5	Temperature
29.0	103°	73.2	290°
50.7	123°	74.0	297°
53.5	130°	74.5	301°
57.5	141°	74.7	304°
65.9	180°	76.3	318°
67.6	200°	77.8	335°
69.8	220°	78.7	350°
70.7	240°	79.0	355°
71.7	260°	80.0	380°
72.4	284°		

In the second series of measurements, we determined vapor pressure dependence on temperature for constant acid compositions using seven samples having P_2O_5 contents ranging from 69.8 to 76.3 wt. %. Measurement results are given in Tables 2, 3, and 4, and are presented graphically in Fig. 3.

The dependence of $\log P$ on $\frac{1}{T}$ for a given composition, and likewise that of $\log a_{H_2O}$ on $\frac{1}{T}$, is not linear (a_{H_2O} was calculated as the ratio of vapor pressure over phosphoric acid to the vapor pressure of water at the same temperature). A linear dependence exists between $\log P$ and phosphoric anhydride content of the acid at constant temperature. Isotherms of this type are shown in Fig. 4. The slope angle of the straight lines with respect to the composition axis changes sharply on transition from aqueous orthophosphoric acid solutions to strong phosphoric acids. Consequently, the relationships between composition, vapor pressure, and temperature must be expressed by different equations for aqueous H_3PO_4 solutions and for a strong phosphoric acids. For strong phosphoric acids, isotherms illustrated in Fig. 4 may be fitted by equations of the form:

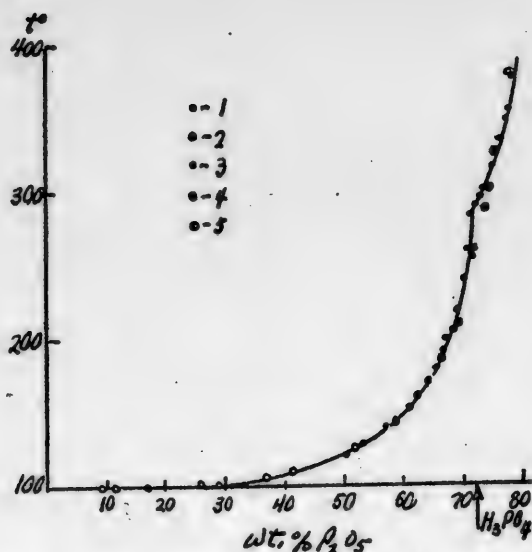


Fig. 2. 1 atm Pressure Isobar for the P_2O_5 - H_2O System. Data sources: 1) Ours; 2) I. Kablukov and K. Zagvozdkin [4]; 3) E. Britske and N. Pestov [5]; 4) Brown and Whitt[8].

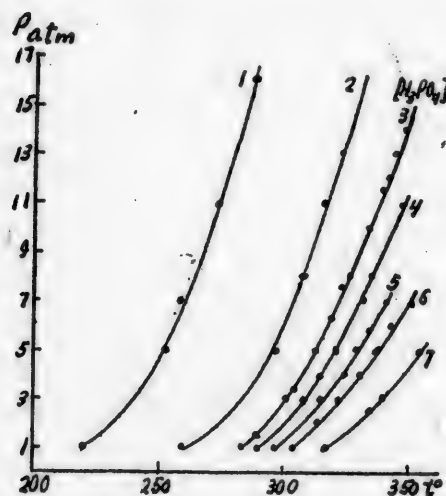


Fig. 3. Dependence of phosphoric acid vapor pressure on temperature. P_2O_5 content: 1) 69.8; 2) 71.7; 3) 72.4; 4) 73.8; 5) 75.0; 6) 76.7; 7) 78.3.

pressure of water vapor over pure H_3PO_4 (i.e., at 72.4 wt. % P_2O_5) at the same temperature; k is a coefficient depending on temperature; ΔC is the difference between water contents of H_3PO_4 and strong phosphoric acid, expressed in weight percent: $\Delta C = 27.6 - \text{wt. \% } H_2O = \text{wt. \% } P_2O_5$.

Values of k calculated by equation (1) are given in Table 5; values of P and P_0 used in the calculations were obtained by graphical interpolation of data in Tables 3 and 4.

A plot of k versus $1/T$ gives a straight line (Fig. 5) which corresponds to the equation:

$$k = \frac{500}{T} - 0.671. \quad (2)$$

TABLE 2
Dependence of Aqueous Orthophosphoric Acid Solution Vapor Pressure on Temperature.

Weight % P_2O_5	Temperature	Vapor Pressure (atm).
69.8	220°	1.0
	253°	5.0
	260°	7.0
	275°	11.0
	290°	16.0
71.7	260°	1.0
	298°	5.0
	309°	8.0
	318°	11.0
	325°	13.0
	345°	20.0

TABLE 3
Dependence of Orthophosphoric Acid Vapor Pressure on Temperature (72.4% P_2O_5).

Temperature	Vapor Pressure (atm).
284°	1.0
290°	1.5
302°	3.0
305°	3.4
214°	5.0
320°	6.3
325°	7.6
327°	8.0
335°	10.0
341°	11.5
343°	12.0
346°	13.0
350°	14.0

$$\log \frac{P}{P_0} = -k\Delta C, \quad (1)$$

where: P is the pressure of water vapor over acid of the given composition; P_0 is the pres-

TABLE 4

Dependence of Strong Phosphoric Acid Vapor Pressure on Temperature

Wt. % P ₂ O ₅	Temperature	Vapor pressure, atm	
		Experimental	According to Equation (3)
73.2	290°	1.0	1.0
	309	3.0	2.9
	315	4.0	3.8
	322	5.0	5.0
	332	7.0	7.0
	336	8.0	7.8
74.0	348	10.8	10.5
	297	1.0	1.1
	316	3.0	2.8
	325	4.0	4.2
	330	5.0	4.9
	335	5.8	5.7
74.7	342	7.0	7.0
	304	1.0	1.1
	315	2.1	2.0
	323	3.0	2.9
	331	4.0	3.9
	338	5.0	4.9
76.3	344	6.0	5.9
	352	7.0	7.3
	318	1.0	1.2
	335	2.5	2.6
	340	3.1	3.1
	355	5.0	5.1

Equations (1) and (2) give:

$$\log \frac{P}{P_0} = \left(0.671 - \frac{500}{T} \right) \Delta C. \quad (3)$$

Experimental values of vapor pressure over strong phosphoric acid are compared with values calculated from Equation (3) in Table 4. The discrepancies do not exceed experimental error. Thus, Equation (3) may be used as an interpolation equation for calculating strong phosphoric acid vapor pressures.

Equation (3) expresses a linear dependence of $\log P$ on P₂O₅ weight percent at constant temperature. Weight percents were used for convenience in calculation; an analogous dependence would be obtained in the given composition range by expressing composition in mole fraction. This kind of dependence is observed in other systems. Thus, for example, the logarithm of HCl vapor pressure (or the logarithm of HCl activity) over concentrated aqueous solutions varies approximately linearly with solution composition, as can be easily demonstrated by examining the corresponding data [12]. These relation-

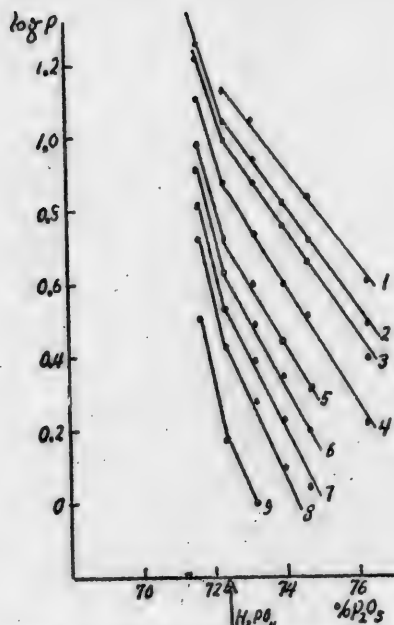


Fig. 4. Isotherms of log pressure versus composition at given temperatures.

1) 350°, 2) 340°, 3) 335°, 4) 325°, 5) 315°, 6) 310°, 7) 305°, 8) 300°, 9) 290°.

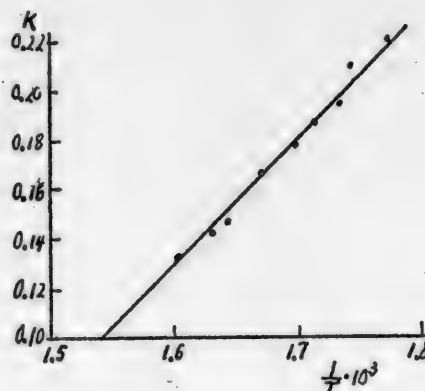
Fig. 5. Dependence of coefficient k on T .

TABLE 5

Temperature Dependence of k

Temperature	k	Temperature	k
290	0.2201	325	0.1662
300	0.2101	335	0.1470
305	0.1945	340	0.1440
310	0.1866	350	0.1331
315	0.1780		

ships can be regarded as a generalization of I. M. Sechenov's law [13].

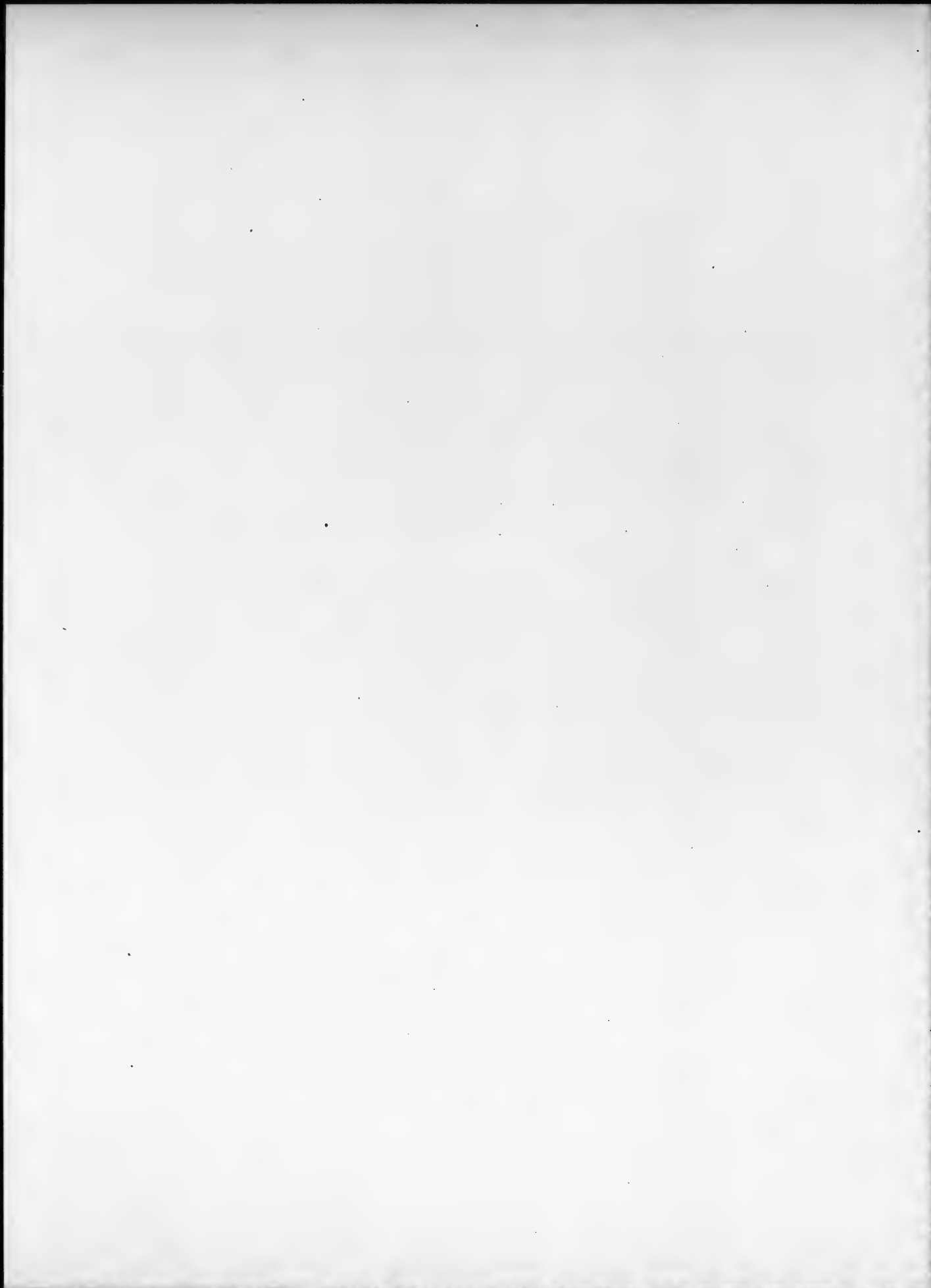
SUMMARY

1. A new method for measuring vapor pressure was developed.
2. Temperatures were measured at which vapor pressures in the $P_2O_5-H_2O$ system were equal to 1 atm in the composition range from 29.0 to 80 wt. % P_2O_5 .
3. A singular point, corresponding to the compound H_3PO_4 (72.4% P_2O_5) was found on the isobar.
4. Vapor pressure dependence on temperature was measured for acids having P_2O_5 compositions ranging from 69.8 to 76.3 wt. % at vapor pressure values from 1 to 20 atm.
5. The logarithm of vapor pressure is a linear function of water content for strong phosphoric acids (i.e., for P_2O_5 content above 72.4%). An interpolation equation is given for calculating vapor pressure of strong phosphoric acids.

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Received April 25, 1953.



THE SYSTEM: $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$

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In the present work, we made an investigation of a system containing beryllium sulfate, ferrous sulfate, and water, in order to explore the nature of the interaction of these salts. It was known from literature data that ferrous sulfate forms solid solutions with sulfate salts of many divalent metals (magnesium, zinc, cadmium, cobalt, nickel and copper). According to data of Klatso [1], ferrous sulfate forms double salts with beryllium sulfate. Our studies of the $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ system were performed at 25 and 60°. The 60° temperature was selected by us because of the condition that ferrous sulfate and beryllium sulfate crystallize as tetrahedra at this temperature, and thus the possibility of forming mixed crystals of these salts would not be excluded. Composition of the third phase was determined by Shreinemakers' residue method and also on the basis of crystallo-optical analysis. Solutions and solid phase were analyzed for iron content by a chromatometric method, the beryllium-xon sum was determined by an alkalimetric method, and the quantity of beryllium calculated from the data obtained. Solution refractive index was measured with an Abbe refractometer. Solution density was determined using pycnometers.

Investigation of the System: $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ at 25°

Refractive indexes for the solid phase of the system under study at 25° are given in Table 1, as determined by us using an immersion method; refractive indexes for $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are noted (taken by us from Winchell's handbook).

TABLE 1.

Refractive index of solid phase (Tests 1,2,3-Table 2)		Refractive index for $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (according to Winchell)	
Ng	Np	Ng	Np
1.1471	1.440	1.472	1.439
Refractive index of solid phase (Tests 5,6,7,8,9-Table 2)		Refractive index for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (according to Winchell)	
Ng	Np	Ng	Np
1.489	1.471	1.486	1.471

By comparing data obtained by us with refractive index values taken from Winchell's handbook for the sulfate salts of beryllium and ferrous iron, we may conclude that the solid phase was $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ in experiments 1,2, and 3 (Table 2) and was $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in experiments 5,6,7,8, and 9 (Table 2). Table 2 and Fig. 1 present results of investigating liquid and solid phase compositions in the $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ system at 25°.

TABLE 2.

System: $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ (25°)

Experiment number	Liquid phase composition (wt. %)			"Residue" composition (wt. %)			4) Bottom phase
	BeSO_4	FeSO_4	H_2O	BeSO_4	FeSO_4	H_2O	
1	28.72	—	71.28	—	—	—	$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$
2	25.53	3.59	70.88	54.52	0.50	44.98	
				51.00	1.13	47.87	
3	24.11	6.54	69.35	—	—	—	$\text{BeSO}_4 \cdot 4\text{H}_2\text{O} + \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
4	24.00	8.09	67.91	39.42	13.25	47.33	
				65.14	15.84	19.02	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
5	21.31	10.72	67.97	—	—	—	
6	17.19	11.60	71.21	1.20	51.45	47.35	
				2.15	49.60	48.25	
7	12.23	14.17	73.60	0.96	51.58	47.46	
				1.02	50.76	48.22	
8	5.73	18.39	75.88	0.50	54.04	45.46	
9	—	22.74	77.26	—	—	—	

Liquid phase densities, refractive indexes and compositions for this same system are given in Table 3. As is shown by the Fig. 2 data, solubility, density, and refractive index isotherms for the solutions consisting of two branches, corresponding to equilibrium of solutions with the salts $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (branches A_2B_2 ; $A'_2B'_2$; $A''_2B''_2$) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (branches B_2C_2 ; $B'_2C'_2$; $B''_2C''_2$).

$\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ system at 60°. Ferrous sulfate solutions oxidize very rapidly at elevated

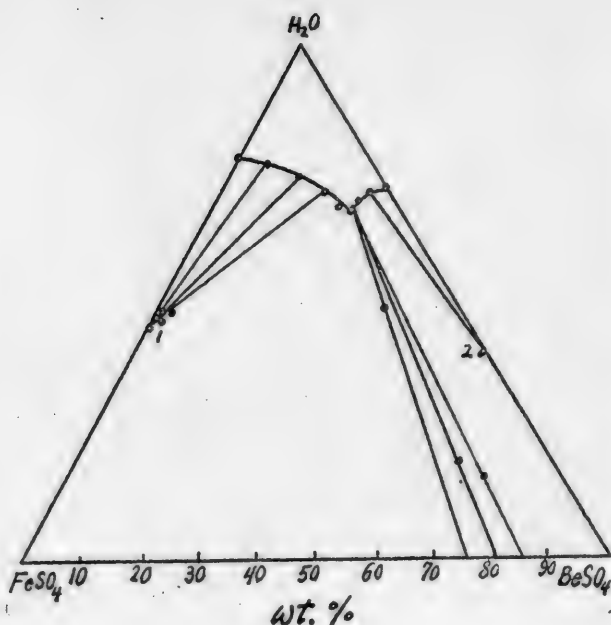


Fig. 1. System $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ at 25° .
1— $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; 2— $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$.

fate. System equilibrium was reached after mixing the solution with excess solid phase for 8-10 hours. Control experiments were performed over a 48 hour period. Solid phases were investigated by Shreinemaker's "residual" method.

TABLE 3.
System: $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ at 25° .

Ex- peri- ment num- ber	d_4^{25}	Liquid phase re- fractive index	Salt composition (%)		Quantity of water in g per 100 g salt
			BeSO_4	FeSO_4	
1	1.285	—	100	—	248.0
2	1.306	1.389	89.06	10.94	243.4
3	—	—	83.93	16.07	226.2
4	1.340	1.393	82.97	17.03	211.7
5	1.312	1.389	73.64	26.36	212.3
6	1.300	1.387	59.84	40.16	247.4
7	1.296	1.385	42.57	57.43	278.8
8	1.282	1.382	19.95	80.05	314.7
9	1.270	1.378	—	100	339.7

ferrous sulfate and beryllium sulfate decrease each other's solubility.

3. Existence of double salts and solid solutions was not observed in the system.

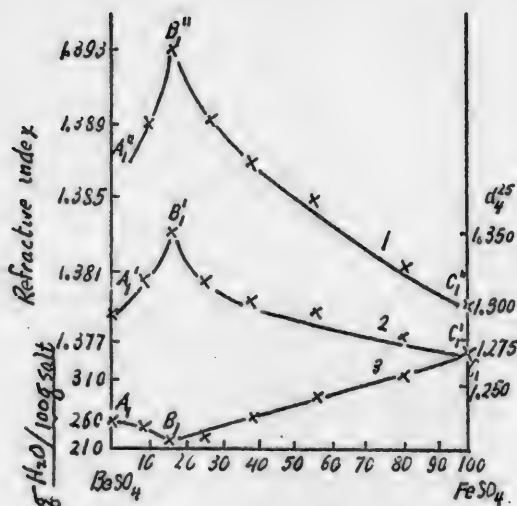


Fig. 2. System $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ at 25° .
1) Refractive index isotherm; 2) density isotherm;
3) solubility isotherm.

temperature. A continuous stream of hydrogen was passed through the solution in order to guard against oxidation. Stability of ferrous sulfate solutions was noticeably increased in presence of beryllium sul-

Compositions of solution and solid phases investigated are given in Table 4.

Solubility isotherms in the system at 60° (Fig. 3) consist of 2 branches, corresponding to crystallization from solution of a solid phase consisting of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$; no double salts or solid solutions were observed at 60° .

SUMMARY

1. Solubility, density, and refractive index isotherms were investigated for the $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ system at 25 and 60° .

2. It was established that

TABLE 4

System: $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ (60°)

Test No.	Liquid phase composition, wt. %			"Residue" composition, wt. %			Bottom phase
	BeSO_4	FeSO_4	H_2O	BeSO_4	FeSO_4	H_2O	
1	—	34.94	65.06	—	1) 65.73 2) 66.70	34.27 33.30	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
2	8.82	25.56	65.62	0.69	61.48	37.83	
3	13.58	21.05	65.37	1) 0.5 2) 0.4	1) 63.0 2) 63.2	36.5 36.4	
4	14.56	20.60	64.84	—	—	—	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O} + \text{BeSO}_4 \cdot 4\text{H}_2\text{O}$
5	20.20	16.68	63.12	1) 18.14 2) 18.15	1) 43.00 2) 43.18	38.86 38.67	
6	20.40	16.70	62.90	14.62	49.11	36.27	
7	20.42	16.50	63.08	35.80	17.88	46.32	$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$
8	34.60	—	65.40	1) 57.04 2) 58.80	— —	42.96 41.20	
9	27.21	6.60	66.19	1) 51.68 2) 52.10	1) 1.11 2) 1.11	47.21 46.79	
10	26.70	7.75	65.55	1) 51.12 2) 51.30	1) 1.90 2) 2.01	46.98 46.69	
11	23.68	10.38	65.94	—	—	—	

4. The solid phases were crystal hydrates of simple salts: $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at 25° ; $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ at 60° .

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Received March 19, 1953. Moscow State University

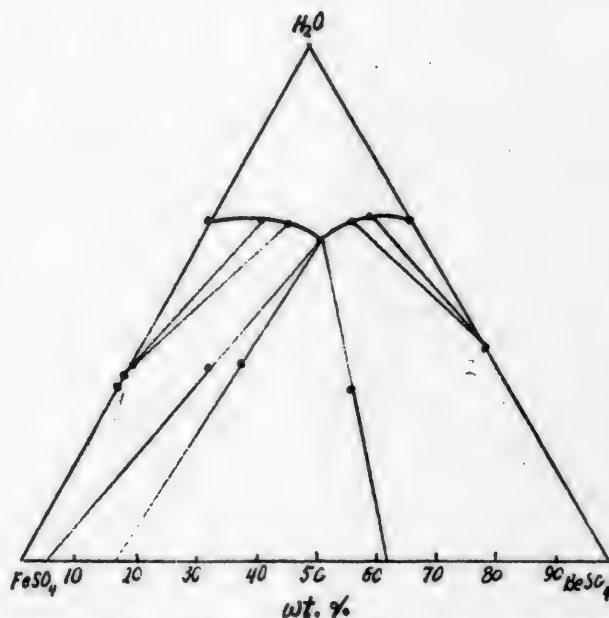


Fig. 3. $\text{BeSO}_4\text{--FeSO}_4\text{--H}_2\text{O}$ at 60° .
1) $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$; 2) $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$.



SYSTEM $\text{BeSO}_4 - \text{MnSO}_4 - \text{H}_2\text{O}$ (25°)

O.I. Vorobyeva and L.R. Osanova

In the present work, we conducted an investigation of an aqueous system containing beryllium sulfate and manganese sulfate, for the purpose of explaining the nature of interaction of these salts.

According to literature data, manganese sulfate forms solid solutions with sulfates of many divalent metals (iron [1], zinc [2], and magnesium [2,3]).

It is noted in a paper by Klatso [4] that manganese sulfate forms mixed crystals of two types with beryllium sulfate: triclinic crystals containing 23.1% MnO and 2.73% BeO; and tetragonal crystals containing 8.41% MnO and 10.44% BeO.

It was later shown by Retgers that each of the salts crystallizes separately and does not form compounds from solutions saturated with beryllium sulfate and manganese sulfate.

Investigation of the $\text{BeSO}_4 - \text{MnSO}_4 - \text{H}_2\text{O}$ system at 25° . Solid phase compositions were determined graphically by the residue method [6] and also on the basis of crystallo-optical analysis. Liquid and solid phases were analyzed for beryllium content alkalimetrically [7], and also gravimetrically as BeO [8]. Manganese was determined by a volumetric procedure, according to Volhard [9]. Solution densities were determined using pycnometers. Based on the data obtained (Tables 1,2), we constructed a solubility isotherm (Fig. 1) and a density isotherm (Fig. 2) for the $\text{BeSO}_4 - \text{MnSO}_4 - \text{H}_2\text{O}$ system at 25° . The isotherms consist of two branches corresponding to crystallization from solution of the solid phases $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. Formation of double salts and solid solutions was not observed in the given system under these conditions.

TABLE 1
 $\text{BeSO}_4 - \text{MnSO}_4 - \text{H}_2\text{O}$ System at 25°

Expt. No.	Liquid phase composition (wt. %)		"Residue" composition (wt. %)		Bottom phase
	BeSO ₄	MnSO ₄	BeSO ₄	MnSO ₄	
1	28.7	—	—	—	BeSO ₄ · 4H ₂ O
2	25.14	4.84	60.10	—	
	—	—	59.90	—	
3	23.14	10.03	46.27	3.02	
	—	—	45.14	3.30	
4	20.67	15.09	not analyzed *		
5	18.64	18.03	45.82	6.18	
	—	—	46.88	5.64	
6	17.00	21.39	45.10	7.71	
	—	—	45.60	7.35	
7	17.29	21.22	39.18	20.33	BeSO ₄ · 4H ₂ O + + MnSO ₄ · 5H ₂ O
	—	—	32.43	21.11	
8	13.66	25.41	6.20	45.00	MnSO ₄ · 5H ₂ O
	—	—	6.20	45.50	
9	7.40	30.05	3.10	46.70	MnSO ₄ · 4H ₂ O
10	5.25	33.00	not analyzed *		
11	—	39.37	—	—	
12	7.48	29.90	5.1	46.13	
13	14.89	24.44	7.00	47.62	
			6.14	49.70	

* Determined by a crystallo-optical method

TABLE 2
 $\text{BeSO}_4 - \text{MnSO}_4 - \text{H}_2\text{O}$ System at 25°
Liquid Phase Densities

Liquid phase composition (mol. %)	d_{25}^4
MnSO_4	
—	1.279
11.80	1.316
23.08	1.358
33.55	1.384
40.20	1.407
46.68	1.430
56.37	1.455
73.97	1.476
100	1.500

In the portion of the system we studied, where the solutions were saturated with manganese sulfate (in the last two tests of Table 1 and in Fig. 1), the bottom phase was a metastable form of manganese sulfate having the composition $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.

With regard to the existence of such a hydrate, there are references by a number of authors [10, 11] who

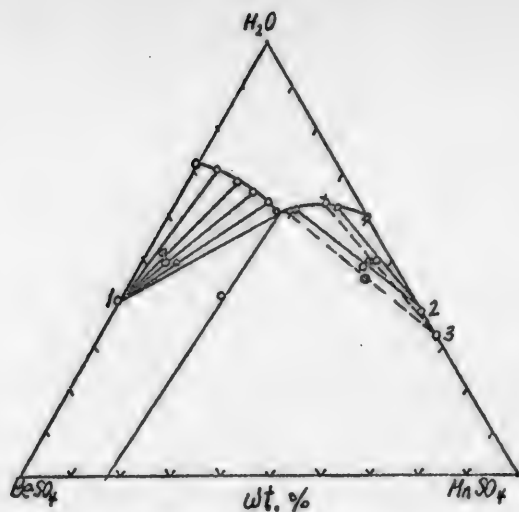


Fig. 1. BeSO_4 - MnSO_4 - H_2O system at 25° .
Solubility isotherms: 1) $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$; 2) $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$;
3) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.

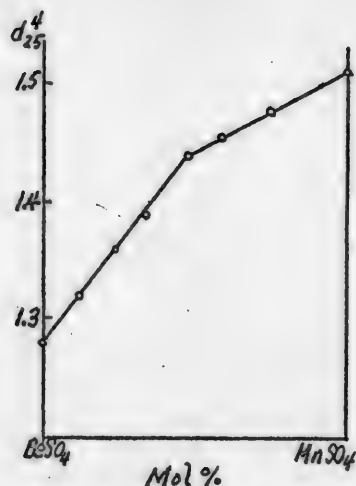


Fig. 2. BeSO_4 - MnSO_4 - H_2O system at 25° .
Liquid phase density isotherm.

were investigating solubility polytherms of manganese sulfate in water.

SUMMARY

1. Solubility and density isotherms for the BeSO_4 - MnSO_4 - H_2O system at 25° were investigated.
2. It was found that beryllium sulfate and manganese sulfate reduce each other's solubility.
3. It was established that the solid phases in the BeSO_4 - MnSO_4 - H_2O system at 25° were $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, and the metastable $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.
4. Formation of double salts or solid solutions was not observed in the system.

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DISTRIBUTION OF ISOMORPHIC AND ISODIMORPHIC COMPONENTS BETWEEN SOLID AND LIQUID PHASES IN CRYSTALLIZATION FROM AQUEOUS SOLUTIONS

I. EQUILIBRIUM AT 20° IN SEVERAL SYSTEMS WITH COMPONENTS OF THE COPPERAS TYPE

G. I. Gorshtein and N. I. Silantyeva

The question of laws for equilibrium distribution of isomorphic components between liquid and solid phases in crystallization from aqueous solutions already arose at the time the Van't Hoff theory of solid solution formation was being developed [1].

Roozeboom [2], continuing the classical studies of the Russian scientist Konovalov [3], in studying the equilibrium between liquid and vapor phases in two component systems, developed the classification of three component systems with two isomorphic components (the third component was solvent, usually water).

These authors directed their attention on the important aspect of studying the quantitative laws for equilibrium distribution of isomorphic components between liquid and solid phases. However, in the course of more than 20 years since they did this, there have been only a few separate attempts [3, 4, 5, 6] to solve this question which, moreover, have not had successful results.

Many cases on studies of different systems with isomorphic and isodimorphic components are limited to the obtaining of tables and diagrams which link equilibrium liquid and solid phase compositions without any theoretical discussion. The lack of a guiding theoretical principle promoted inadequate reliability in many experimental investigations of systems with isomorphic components. The first fundamental change of position in this field was connected with the appearance (about 1924) of the classical studies by the Khlopin school [7] (Khlopin, Nikitin, Polesitsky, Ratner, and others) on studying equilibrium distribution of actual isomorphic microcomponents during crystallization of salts from water solutions.

As a result of further investigations, the linear rule for distribution of isomorphic impurities was established. Radioactive substances were used as microcomponents; this facilitated obtaining rapid and also sufficiently accurate results. The Khan school [8] conducted work in this direction.

According to the Khlopin rule, the equilibrium distribution of an isomorphic or isodimorphic microcomponent is characterized by a constant D_{eq} - the ratio of the microcomponent concentration in the solid phase to its concentration in the solute portion of the mother liquor [D_{eq} is usually here called the equilibrium distribution coefficient, but the terms crystallization coefficient (Khlopin) and coefficient of isomorphic mixing (Chirkov) are also employed].

Ratner [9] presented a thermodynamic theory for equilibrium distribution of isomorphic microcomponents between solid and liquid phases.

The most important achievement of this paper was the development of a very rapid, and at the same time reliable, method for attaining equilibrium of specific microcomponents between liquid and solid phases. Studies of the Khlopin school were conducted at very low concentrations of the isomorphic component - of the order of 10^{-12} to 10^{-3} mol.%. In Chirkov's studies [10] on distribution of Br⁻ or I⁻ impurities in crystallizing potassium, sodium, and magnesium chlorides from aqueous solutions, the Khlopin distribution rule was confirmed for microconcentrations to about 1.5% in the solute portion of the mother liquor.

There remains, naturally, the open question on the laws of component distribution during transition from micro- to macroconcentrations, and the question on the general nature of equilibrium distribution curves.

Attempts have been made [14] to express the distribution curves by the formula $y_A = x_A^m$, where x_A is concentration of any component A in solute portion of mother liquor; y_A is concentration of the same component in

solid phase; \underline{m} is a constant, characteristic of the given system at a given temperature. In actuality, this empirical formula does not have a general character, because it gives $\frac{dy_A}{dx_A} = 0$ or $\frac{dy_A}{dx_A} = \infty$, for microconcentrations of component A, whereas the value of $\frac{dy_A}{dx_A}$ is equal to D_{eq} for microconcentrations.

Evidently, for ordinary methods of expressing component concentrations in the solid phase and in the solute portion of the mother liquor, the Khlopov linear distribution law may be applicable only for a very restricted narrow portion of the equilibrium curve.

However, the concentration of one component A may be expressed as a ratio to the concentration of the other component B in the same phase, and we may interpret as the equilibrium distribution coefficient of component A, the ratio of these "relative" concentrations for component A in the solid phase and in the mother liquor:

$$D_{eq}(A, B) = \frac{y_A}{y_B} \cdot \frac{x_B}{x_A}$$

Then the $D_{eq}(A, B)$ value, or its reciprocal $D_{eq}(B, A)$, may be constant not only for microconcentrations of one component, but also over a wide interval of macroconcentrations and even for the entire range of component concentrations. Systems for which the D_{eq} value is constant, appear "ideal" at any concentration of components or in definite regions of component concentration corresponding to a concentration interval having a constant D_{eq} value. In the particular case in which the $D_{eq}(A, B)$ value is equal to unity (the equilibrium curve lies along the the diagram diagonal), the system is "congruent".

For ideal systems, the usual distribution diagram curves have hyperbolic shape, expressed analytically as:

$$y_A = \frac{100 D_{eq} x_A}{100 - x_A (1 - D_{eq})}$$

where x_A and y_A are concentrations of component A in solute portion of mother liquid and in solid phase; D_{eq} is the equilibrium distribution coefficient value for component A as compared with component B.

Generalizing the meaning of equilibrium distribution coefficient for microconcentrations and for macroconcentrations of the components ensues also from thermodynamic development of the equilibrium distribution question made by Shlezinger and Zorkina [11], Hill, Durham, and Ricci [12], and by Shishkin [13]. Hill and his coworkers studied equilibrium distribution of isomorphic components in several systems with double salts of the alum and schoenite types; however, the experimental data they obtained are in part incompletely reliable, and together with this, conclusions with regard to ideality of the systems under study are not always sufficiently established. The authors do not use the D_{eq} value, but rather its logarithm, which tends to cover the nonuniform scattering of D_{eq} determination results.

Activity formulas obtained for D_{eq} by various authors on a theoretical thermodynamic basis differ from one another, as a rule, only in methods of expressing concentrations and activity coefficients. For systems with ionic crystals, we regard as most suitable the formula in which activity coefficients do not appear for the separate ions in solution, but rather the average activity coefficient of the components—according to Lewis [15].

$$D_{eq}^{v+}(A, B) = \left(\frac{L_B}{L_A} \cdot \frac{\gamma_0^{v+} B^+}{\gamma_0^{v+} A^+} \right) \cdot \frac{\gamma_{+A}^v}{\gamma_{+B}^v} \cdot \frac{\gamma_{SB}^{v+}}{\gamma_{SA}^{v+}} \quad (1)$$

Where: L) solubility product of the pure components; v) total number of ions into which the molecules of each component electrolytically dissociate; v^+) is the number of non-common ions obtained on dissociating molecules of both components; γ_0^{\pm}) is the average activity coefficient for each component in pure saturated solution; γ_{\pm}) is the average activity coefficient for each component in equilibrium with solid phase in mother liquor containing both components; γ_S is the activity coefficient for each component in the solid solution; here the standard state ($\gamma_S = 1$) corresponds to taking the component as a pure solid phase.

In formula (1) the product taken in parenthesis has a constant value independent of the ratio of component concentrations.

In the event of isodimorphism, the solubility product corresponds to those modifications of each component which appear in the solid solution.

Thus, deviation of the system from ideality is connected with changes in the ratios:

$$\frac{\gamma_{+A}}{\gamma_{+B}} \text{ and } \frac{\gamma_{SB}}{\gamma_{SA}}$$

In cases when the non-common ions of isomorphous components have similar radii measurements (which is common), identical types of external electronic shells, and also with components which are not too strongly different in solubility, we may expect that:

$$\frac{\gamma_{+A}}{\gamma_{+B}} = 1 \text{ and } \frac{\gamma_{SB}}{\gamma_{SA}} \approx 1.$$

Then the system will be approximately ideal for the case of isomorphous components in any ratio, and in the event of isodimorphism — in the region of existence of solid solutions having certain structures. Calculation of the D_{eq} value for individual points connecting compositions of solid and liquid phases, based on experimental data, does not pose particular difficulty.

Things are otherwise with regard to the possibility of determining the D_{eq} value from the thermodynamic formula (1). Even for ideal systems, calculation of D_{eq} by this formula is associated with major complications, in view of the absence of experimental data on activity coefficients for electrolytes in saturated aqueous solutions. It is even more difficult to take account of the system's deviation from ideality in connection with activity coefficients for individual components in the mother solution and solid phases. Together with this, the possibility of forecasting the degree of entraining specific isomorphous impurities in crystallizing any salt from an aqueous solution has important practical significance. In isomorphism, components less soluble than the salt usually tend to enter the solid phase to a larger degree than more soluble salts, but there may even be exceptions on account of corrections connected with the activity coefficients of the components. In isodimorphism, this criterion generally loses significance — if one does not consider the seldom known solubility of metastable modifications of the components.

The D_{eq} value is more or less dependent on temperature. Character and composition of the solvent may also have areal effect on the D_{eq} value; in certain cases solution pH and addition of complex formers promote changes in activity coefficients of components in solution. One of us [16] has discussed two rules, which enable approximate calculation of D_{eq} values in a number of cases for systems which have not been studied experimentally.

First rule. For isomorphous substances which form a congruent system at the given temperature (third component — solvent), any isomorphous or isodimorphous impurities come down in approximately the same degree during crystallization from solution.

For small deviations from congruence, we may introduce appropriate correction, bearing in mind the fact that the greater the transition of a substance into the solid phase, the less the degree to which any isomorphous or isodimorphous impurity is carried down.

Second rule. If values of the equilibrium distribution coefficients are known for an ideal system containing the isomorphous components A and B and for one containing components B and C, then one may find the D_{eq} value for an ideal system containing components A and C by the formula:

$$D_{eq} (A, C) = D_{eq} (A, B) \cdot D_{eq} (B, C).$$

The second rule can be readily obtained from formula (1); the first rule arises from the similarity of properties of components forming a congruent system.

In our previously published investigation [16] on distribution of impurities during crystallization of inorganic salts, it was confirmed that the Khlopin linear distribution rule was applicable and D_{eq} values were found for various systems with isomorphous and isodimorphous components.

It was also shown there that certain systems with isomorphous and isodimorphous components were ideal over a wide component concentration interval.

In the present contribution, we present results of studying a number of systems with two isomorphous or isodimorphous components which were performed over the entire interval of concentration for both components for the purpose

of exploring the laws of equilibrium distribution between solid and liquid phases;

Methods for Studying Equilibrium between Solid and Liquid Phases in Systems with Isomorphic Components

The question of methods for attaining equilibrium between solid and liquid phases in systems with isomorphic or isodimorphic components is associated with special difficulties which are not encountered in study of systems with nonisomorphic components.

The numerous variants of the method of study may be subdivided into two groups: 1) "recrystallization" methods—involving lengthy agitation of crystals of both components with the solution at various starting ratios for the components in the solid and liquid phases, and 2) methods of crystallization from supersaturated solutions under varying conditions of performing the crystallization processes. In the event the former methods are used, equilibrium is attained as a result of a very slow process of recrystallization. Duration of the experiments is large, generally of the order of several weeks, and in a number of cases it is nevertheless difficult to obtain reliable results.

In using methods of crystallization from supersaturated solutions by cooling hot concentrated solutions or by isothermally evaporating, they try to perform the experiment with a very small degree of separation of the substance into the solid phase—with a total degree of crystallization not greater than about 5%. This causes significant prolongation of the experiments.

In using methods of crystallization from supersaturated solution, they do not always consider the important significance of the conditions for performing the crystallization process.

One of us [17] gave a theoretical treatment of the problem of deviation from equilibrium distribution of isomorphic components in relation to the methods and conditions of crystallization from supersaturated solutions. On the basis of this study, it can be shown that a small total degree of crystallization of the substance does not always guarantee a sufficient approximation to the equilibrium state.

The Khlopins school, in studying distribution of isomorphic microcomponents during crystallization of salts from aqueous solutions, developed a remarkably rapid method for attaining equilibrium between solid and liquid phases—a method of relieving supersaturation isothermally with energetic agitation [7]. Equilibrium is usually reached by this method in 4–5 hours.

This method for reaching equilibrium was widely used by us for studying systems with macroconcentrations of both isomorphic components.

After performing the crystallization operation, analyses were made for both isomorphic components in the initial solution, the mother liquors, and the crystals separated from the mother liquors. Solid phase composition was calculated using a formula derived on the basis of Shreinemaker's method of residues.

$$C_{SA} = \frac{C_{CA} - \frac{C_{MA} - C_{CA}}{C_{CB} - C_{MB}} \cdot (100 - C_{CB})}{1 - \frac{C_{MA} - C_{CA}}{C_{CB} - C_{MB}}}$$

where C_{SA} is the concentration of component A in the solid phase (%); C_{MA} and C_{MB} are concentrations of components A and B in the mother liquor (%); C_{CA} and C_{CB} are concentrations of components A and B in the crystals (%).

The $D_{eq}(A, B)$ value is calculated by the formula:

$$D_{eq}(A, B) = \frac{C_{SA}}{100 - C_{SA}} \cdot \frac{C_{MB}}{C_{MA}}$$

Equilibrium in the $FeSO_4-COSO_4-H_2O$ system at 20°. Both isomorphic components form heptahydrated salts at 20° in the monoclinic system. The concentration of $FeSO_4 \cdot 7H_2O$ in the crystals and mother liquors was determined by titrating with potassium permanganate; concentration of $CoSO_4 \cdot 7H_2O$ was determined by potentiometric titration with potassium ferricyanide.

Experimental results are given in Table 1, in the equilibrium composition diagram (Fig. 1), and in the component distribution diagram (Fig. 2). The system is ideal for the entire concentration interval for each component (from 0 to 100% in the solute portion of the mother liquor). The $D_{eq}(Fe, Co)$ value was 1.20. The $D_{eq}(Co, Fe)$ value was 0.84.

TABLE 1

Experiment number	Analytical results on crystals (%)		Analytical results on mother liquors		% $FeSO_4 \cdot 7H_2O$ In solid phase	% $FeSO_4 \cdot 7H_2O$ In solute portion of mother liquor	Distribution coefficient	
	$CoSO_4 \cdot 7H_2O$	$FeSO_4 \cdot 7H_2O$	$CoSO_4 \cdot 7H_2O$	$FeSO_4 \cdot 7H_2O$			$D(Co, Fe)$	$D(Fe, Co)$
1	—	—	48.16	—	0.00	0.00	—	—
2a	82.90	9.59	38.81	3.77	10.43	8.86	0.83	1.20
2b	82.32	9.56	38.80	3.81	10.51	8.94	0.83	1.20
3	71.85	20.81	34.92	8.54	22.65	20.72	0.84	1.19
4a	58.16	34.32	27.68	13.84	37.33	33.33	0.84	1.19
4b	58.22	34.32	27.97	13.59	37.35	32.72	0.81	1.23
5a	55.19	39.43	25.71	15.45	41.85	37.55	0.83	1.20
6a	29.77	65.17	13.89	25.71	68.79	64.92	0.84	1.19
6b	29.79	64.12	14.29	25.89	68.45	64.43	0.83	1.20
7a	17.78	76.93	8.09	29.67	81.32	78.07	0.84	1.19
7b	17.97	78.24	8.00	29.47	81.38	78.64	0.84	1.19
8	—	—	—	37.05	100.00	100.00	—	—

The system may be regarded as approximately congruent because the D_{eq} value does not deviate much from unity and because the distribution curve (Fig. 2) falls almost on the diagonal. The relationship of the $FeSO_4 \cdot 7H_2O$ concentration in the mother liquor $-C_{Fe}-$ to the $CoSO_4 \cdot 7H_2O$ concentration $-C_{Co}-$ is expressed on the equilibrium composition diagram by a straight line whose equation is $\frac{C_{Fe}}{C_{Fe}^0} + \frac{C_{Co}}{C_{Co}^0} = 1$, where C_{Fe}^0 and C_{Co}^0 are solubilities of the pure starting components.

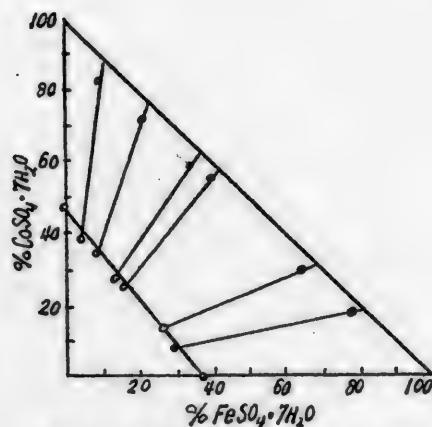


Fig. 1. Equilibrium in $FeSO_4-CoSO_4-H_2O$ system at 20°.

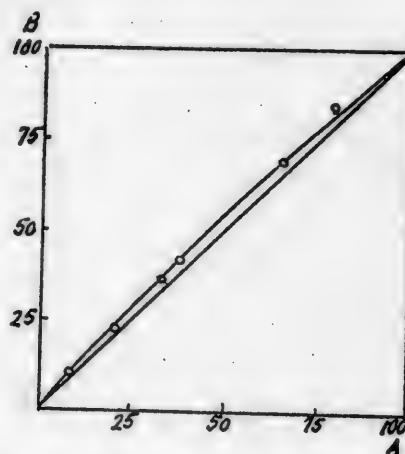


Fig. 2. Distribution curve for components of the $FeSO_4-CoSO_4-H_2O$ system at 20°.

- A) % $FeSO_4 \cdot 7H_2O$ in solute portion of mother liquor
B) % $FeSO_4 \cdot 7H_2O$ in solid phase.

Equilibrium in the $\text{FeSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$ system at 20° . Both components crystallize at 20° as heptahydrated salts; however, ferrous sulfate forms crystals in the monoclinic system while nickel sulfate is in the rhombic system. Consequently, both salts are isodimorphic at 20° . The $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration was determined in the mother liquors and crystals by titrating with potassium permanganate. The $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ concentration was determined by a gravimetric procedure—precipitating with dimethylglyoxime after first oxidizing Fe^{++} to Fe^{+++} using hydrogen peroxide.

As can be seen from Table 2 and from the digram (Fig. 3), two solid solution regions are obtained in the system at 20° : one with a rhombic structure of the $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ type and one with a monoclinic structure of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ type. Each of the stated regions is ideal and is characterized by a constant distribution coefficient value. For the $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ type solid solution region (the iron salt plays the part of an impurity), the equilibrium distribution coefficient value for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $D_{\text{eq}}(\text{Fe}, \text{Ni})$, was found to be 0.50; for the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ type solid solution region (the nickel salt plays the part of an impurity), $D_{\text{eq}}(\text{Ni}, \text{Fe})$ was obtained and = 0.41.

Deviation from ideality in either region does not exceed $\pm 5\%$ relative. The relationship between concentrations of the components in saturated solutions in both regions is expressed by straight lines (Fig. 3). These two lines intersect in an invariant point. The equation for the straight line in the region of existence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ type solid solutions of the monoclinic system is:

$$\frac{C_{\text{Fe}}}{C_{\text{OFe}}} + \frac{C_{\text{Ni}}}{C_{\text{ONi}}} = 1,$$

where C_{Fe} and C_{Ni} are concentrations of FeSO_4 and NiSO_4 in the mother liquors, C_{OFe} is the FeSO_4 concentration in a saturated ferrous sulfate solution, and C_{ONi} is the concentration of a saturated solution of a metastable monoclinic nickel sulfate modification. An analogous kind of equation was obtained for the region of existence of the rhombic system $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ type solid solutions. By extrapolating the solubility line for the solid solutions until they intersect the coordinate axes, it is possible to obtain approximate solubility values for metastable modifications of both salts, namely ferrous sulfate in the rhombic system and nickel sulfate in the monoclinic system.

Experimental results for the $\text{NiSO}_4\text{-FeSO}_4\text{-H}_2\text{O}$ system at 20° enable confirming, for one particular case, the applicability of the first of two previously stated rules for approximately calculating equilibrium distribution coefficient values for isomorphous impurities. As was shown earlier, the $\text{FeSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ system could be considered approximately congruent at 20° with a deviation of 15% from congruence (the cobalt salt enters the solid phase to a smaller degree). According to the first rule, the equilibrium distribution coefficient for any isomorphous or isodimorphic impurity in crystallizing ferrous sulfate must amount to about 0.85 of the equilibrium distribution coefficient value for the same impurity in crystallizing cobalt sulfate.

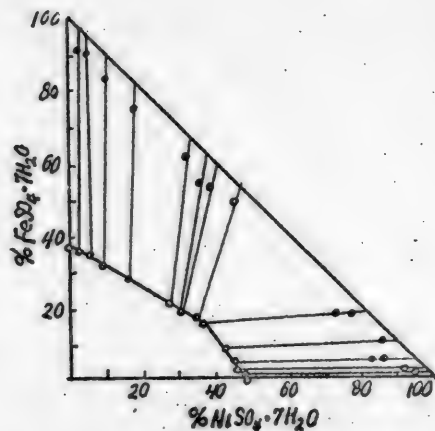


Fig. 3. Equilibrium in the $\text{FeSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$ system at 20° .

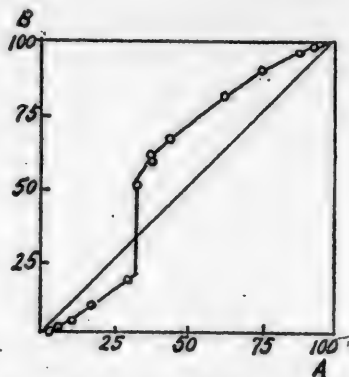


Fig. 4. Distribution curve for components of the $\text{FeSO}_4\text{-NiSO}_4\text{-H}_2\text{O}$ system at 20° . A) % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in solute portion of mother liquor; B) % $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in solid phase.

In a previously published paper [16], it was found that the D_{eq} value for Ni as an impurity in crystallizing cobalt sulfate at 20° was equal to 0.53. The D_{eq} value for Ni as an impurity in crystallizing ferrous sulfate would then be determined, according to the first rule, as $0.53 \cdot 0.85 = 0.45$.

TABLE 2

Test No.	Analytical results (%)					
	Starting solution		Crystals		Mother liquor	
	FeSO ₄ ·7H ₂ O	NiSO ₄ ·7H ₂ O	FeSO ₄ ·7H ₂ O	NiSO ₄ ·7H ₂ O	FeSO ₄ ·7H ₂ O	NiSO ₄ ·7H ₂ O
1	2	3	4	5	6	7
1	—	—	—	—	—	49.20
2a	0.99	52.54	1.20	95.00	1.29	47.85
2b	0.99	52.54	1.27	94.21	1.30	48.10
3a	2.36	51.12	2.32	91.86	2.34	46.48
3b	2.36	51.12	2.41	93.80	2.36	46.66
4a	5.12	51.07	5.45	86.47	5.13	43.82
4b	5.12	51.07	5.51	89.96	5.13	43.28
5a	4.84	53.14	5.17	85.03	4.87	44.96
5b	4.84	53.14	5.07	82.94	4.92	45.24
6a	9.23	47.20	10.03	85.91	9.08	42.69
6b	9.23	47.20	9.93	85.31	9.19	42.79
7a	16.33	43.44	18.34	77.55	16.27	36.40
7b	16.33	43.44	18.29	72.83	16.19	36.33
8a	20.30	35.92	49.28	44.70	16.75	34.69
8b	20.30	35.92	49.54	45.31	16.83	34.92
9a	22.68	31.00	52.29	39.49	18.61	29.72
9b	22.68	31.00	54.18	36.05	18.20	30.42
10a	32.89	29.05	61.38	32.39	21.18	27.23
10b	32.89	29.05	61.43	32.62	21.30	27.26
11a	35.69	16.67	75.01	18.42	27.70	16.41
11b	35.69	16.67	75.08	18.75	27.60	16.31
12a	40.49	9.18	82.58	10.09	31.78	9.24
12b	40.49	9.18	83.44	10.02	31.92	9.09
13a	42.09	6.82	89.59	4.99	34.94	4.50
13b	42.09	6.82	88.58	5.08	35.04	4.47
14a	44.40	2.45	91.05	2.75	36.40	2.46
14b	44.40	2.45	91.21	2.76	36.22	2.47
15	—	—	—	—	37.05	—

As a result of studying the NiSO₄-FeSO₄-H₂O system, a \bar{D}_{eq} (Ni, FeSO₄·7H₂O) value of 0.41 was experimentally obtained; this agrees sufficiently satisfactorily with results from calculation by the first rule.

Equilibrium in the NiSO₄-MgSO₄-H₂O system at 20°. This system was studied by Benrath and Neumann [18] at temperature of 0, 35, 40, 45, 60, 75, 80, and 100°. In their studies, these authors used a "recrystallization" method for attaining equilibrium; in this, crystals and solution were stirred for about 4 weeks with periodic crushing of the crystals for renewing their surfaces. The authors only give tables of composition for the crystals and mother liquors; they do not present solid phase compositions, an equilibrium composition diagram, or a component distribution diagram. This makes it difficult to judge the degree of reliability of the experimental results.

We calculated solid phase compositions from the work of Benrath and Neumann by the Shreinemaker method of residues, and determined distribution coefficient values of the components at individual points.

As an example, we give results of our calculations on the Benrath and Neumann data for temperatures of 0° and 35°.

At a temperature of 0°, both salts are isomorphic (heptahydrated rhombic system).

As can be seen from Table 3, the equilibrium distribution coefficient value for either component, for example the magnesium salt, $-\bar{D}_{eq}$ (Mg, Ni)—varies in a non-uniform manner from 0.42 to 1. This phenomenon is observed even to a greater extent at 35°, as shown in Table 4 in which the results of calculating at this temperature are given.

Thus, despite the long duration of the Benrath and Neumann experiments, their results should be regarded as of low reliability. We investigated this system only at the single temperature of 20° (the components are isomorphic

α total	%FeSO ₄ ·7H ₂ O in solid phase	%FeSO ₄ ·7H ₂ O in solute portion of mother liquor	Distribution coefficient D		Remarks
			D _{Fe, Ni}	D _{Ni, Fe}	
8	9	10	11	12	
—	0.00	0.00	—		Solid solutions with rhombic structure of the Ni SO ₄ ·7H ₂ O type.
0.17	1.20	2.62	0.45		
0.16	1.27	2.63	0.48		
0.17	2.32	4.79	0.47		
0.16	2.41	4.81	0.49		
0.25	5.51	10.49	0.50		
0.27	5.54	10.60	0.49		
0.28	5.25	9.75	0.51		
0.27	5.11	9.80	0.49		
0.17	10.12	17.54	0.53		
0.16	10.00	17.68	0.52		
0.26	18.54	30.88	0.51		
0.27	18.80	30.84	0.52		
		Average . . .	0.50		Solid solutions with monoclinic structure of the FeSO ₄ ·7H ₂ O type.
0.17	51.59	32.56		0.45	
0.16	53.45	32.52		0.42	
0.19	58.75	38.50		0.44	
0.18	61.26	37.43		0.38	
0.42	66.91	43.75		0.38	
0.42	66.69	43.86		0.39	
0.28	81.31	62.79		0.39	
0.29	80.95	62.85		0.40	
0.29	89.79	77.47		0.39	
0.29	89.86	77.83		0.40	
0.32	94.96	88.59		0.41	
0.31	94.85	90.68		0.43	
0.28	97.81	93.66		0.42	
0.28	97.21	93.57		0.42	
—	100.00	100.00	Average . .	0.41	

TABLE 3

Mol. % MgSO ₄		D _{eq} (Mg, Ni)	D _{av} (Mg, Ni)
In solute portion of mother liquor	In solid phase		
91.8	89.5	0.76	0.69
94.1	77.6	0.65	
75.4	69.2	0.73	
59.2	59.2	1.00	
50.7	41.0	0.68	
43.0	28.0	0.83	
31.8	12.5	0.47	
21.0	9.0	0.42	

at this temperature); one of our purposes was to investigate the possibility of obtaining sufficiently reliable results by using the rapid Khlopin method for attaining equilibrium.

The mother liquors and crystals were analyzed in the following manner. The NiSO₄·7H₂O content was determined by electrolyzing nickel from a solution containing

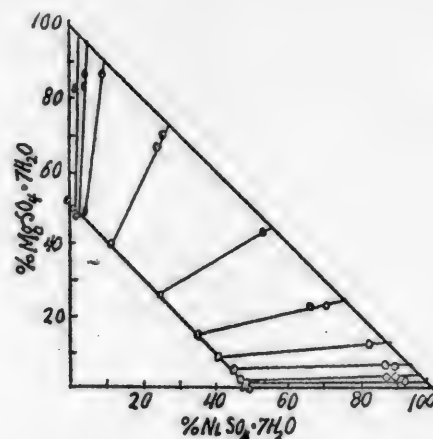
Fig. 5. Equilibrium in the NiSO₄-MgSO₄-H₂O system at 20°.

TABLE 4

Mol. % MgSO_4		D_{eq}	D_{av}
In solute portion of mother liquor	In solid phase	(Mg. Ni)	(Mg. Ni)
97.7	83.0	0.11	
94.1	93.5	0.9	
94.1	97.5	0.44	
80.4	75.5	0.76	
72.8	76.0	1.19	
64.0	56.0	0.72	
55.0	47.0	0.73	
47.0	36.7	0.65	0.62
36.2	27.0	0.57	
26.2	14.2	0.47	
24.3	14.5	0.53	
22.3	13.5	0.56	
20.2	11.7	0.52	
17.7	11.0	0.58	

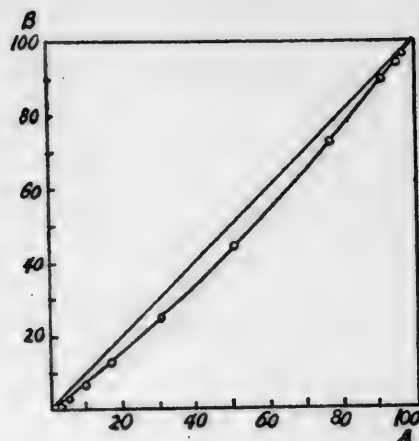


Fig. 6. Distribution curve for components in the NiSO_4 - MgSO_4 - H_2O system at 20° . A) % $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in solute portion of mother liquor; B) % $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in solid phase.

TABLE 5

Test		Analytical results (%)						α total	% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$		Distribution coefficient (D) $D_{\text{Mg, Ni}}$
No	Starting solution		Crystals		Mother liquor		in solid phase		in solute portion of mother liquor		
	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$					
1	—	—	—	—	—	49.20	—	0.00	0.00	—	
2a	1.22	48.54	1.53	91.38	1.20	47.60	0.32	1.59	2.50	0.64	
2b	1.22	48.54	1.61	92.09	1.21	48.54	0.29	1.67	2.47	0.68	
3a	2.43	51.92	3.01	88.25	2.31	47.10	0.18	3.16	2.55	0.66	
3b	2.43	51.92	3.06	89.03	2.29	46.83	0.19	3.02	2.50	0.64	
4a	5.09	56.62	6.37	87.27	4.62	45.02	0.39	6.62	9.28	0.69	
4b	5.09	56.62	6.19	89.27	4.65	44.87	0.39	6.34	9.39	0.65	
5a	11.21	50.58	12.27	81.82	8.60	40.92	0.39	12.38	17.38	0.70	
5b	11.21	50.58	12.25	81.61	8.68	41.37	0.38	12.76	17.18	0.70	
6a	—	—	23.07	69.93	15.44	35.49	—	24.35	30.31	0.74	
6b	—	—	21.71	66.05	15.37	35.21	—	23.81	30.37	0.72	
7a	—	—	43.43	52.99	26.27	24.89	—	44.78	51.31	0.77	
7b	—	—	43.24	52.81	26.38	25.20	—	44.74	51.22	0.77	
8a	45.27	12.72	67.44	24.31	39.85	11.17	0.25	73.01	78.10	0.76	
8b	45.27	12.72	70.27	24.57	39.85	11.15	0.25	73.85	78.10	0.79	
9a	53.61	4.51	86.68	8.95	48.59	4.11	0.20	90.56	92.21	0.81	
9b	53.61	4.51	85.97	8.79	48.72	4.08	0.20	90.62	92.29	0.80	
10a	—	—	85.52	4.08	47.70	1.94	—	95.35	96.00	0.83	
10b	—	—	83.92	4.15	47.55	1.97	—	95.18	96.00	0.81	
11	—	—	83.40	2.31	50.17	1.19	—	97.22	97.70	0.83	
12	—	—	—	—	51.37	—	—	100.00	100.00	—	

excess ammonia with added ammonium sulfate. Electrolysis was performed at a voltage of 16 V and with a current strength of about 3 A. Platinum gauze was used for the electrodes. The electrolyte was agitated using an electromagnetic stirrer. Duration of electrolysis amounted to 40-60 minutes. The $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ content was determined in the solutions after electrolysis by precipitating twice with diammonium phosphate with subsequent

weighing as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ according to the Vasilyev and Sinkovskaya method [19].

Experimental results are given in Table 5 and in Figures 5 and 6.

The equilibrium distribution coefficient value for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ remained constant at a level which averaged 0.65 with changes in concentration of this component in the solute portion of the mother liquor from zero to about 10%.

With further increase in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ concentration, the D_{eq} (Mg, Ni) value smoothly rose to 0.81, which was held for the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ concentration interval from 90 to 100% [the corresponding D_{eq} (Ni, Mg) value for this concentration interval was equal to the reciprocal, 1.23].

Thus, this system has two narrow regions of "ideality" corresponding to a concentration up to 10% of each component in the solute portion of the mother liquor. Deviation from ideality in the middle portion of the equilibrium diagram does not have too abrupt a character and is caused by differences in activity coefficients for both components in one of the phases, or in both of the phases at the same time.

This depends, possibly, on the difference in the polarization properties of Mg^{++} and Ni^{++} ions in connection with the structure of their external electronic shells. The relation between concentrations of both components in the mother liquors is expressed by straight lines on the equilibrium composition diagram. The results we obtained from studying the NiSO_4 - MgSO_4 - H_2O system show that the rapid Khlopin method for attaining equilibrium which was used by us was fully reliable, as contrasted with the method used by Benrath and Neumann.

SUMMARY

1. Equilibrium distribution of isomorphic and isodimorphic components was studied in the FeSO_4 - CoSO_4 - H_2O , NiSO_4 - FeSO_4 - H_2O , and NiSO_4 - MgSO_4 - H_2O systems at 20°; we widely used (for the first time for study of systems at macroconcentrations of isomorphic components) the rapid method for attaining equilibrium developed by Khlopin's school for microconcentrations of one isomorphic component.

2. It was found that the FeSO_4 - CoSO_4 - H_2O system at 20° was ideal. The D_{eq} (Fe, Co) value was found to equal 1.20; the reciprocal, D_{eq} (Co, Fe) was equal to 0.84.

3. It was found that there were two regions for existence of solid solutions of different structure in the NiSO_4 - FeSO_4 - H_2O system with isodimorphic components; in each of these regions the system was ideal. The D_{eq} (Ni, Fe) value in the region of existence of the monoclinic system ferrous sulfate type solid solution (nickel salt - impurity) was found to equal 0.41; the D_{eq} (Fe, Ni) value for the region of existence of the rhombic system nickel sulfate type solid solution (iron salt - impurity) was found to equal 0.50.

4. It was found that the NiSO_4 - MgSO_4 - H_2O system at 20° was ideal only in limited concentration intervals at the ends of the equilibrium composition diagram. Deviation from ideality in the middle portion of the diagram did not have an abrupt character. The equilibrium distribution coefficient value for Mg as an impurity in crystallizing nickel sulfate was found at 20° to be 0.65; the equilibrium distribution coefficient value for Ni as an impurity in crystallizing magnesium sulfate was found to be 1.23.

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Received November 15, 1952.

* See Consultants Bureau English Translation, p. 1025.



COPPER COMPLEXES WITH DIMETHYLGLYOXIME

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A complex compound of copper and dimethylglyoxime, as well as with other dioximes, was first separated by L. A. Chugaev [1] in 1905; he showed that this compound was analogous to nickel dimethylglyoxime in some of its properties and that its composition could be expressed by the formula $\text{Cu}(\text{HDm})_2$, where HDm^- is a singly charged dimethylglyoxime anion. The compound $\text{Cu}(\text{HDm})_2$ was also investigated by V. M. Peshkova [2].

The properties of $\text{Cu}(\text{HDm})_2$ have been only slightly studied although knowledge of the properties of this compound, as the first of a large class of internal complex compounds—the dioximes—has significance for the chemistry of complex compounds as well as for analytical chemistry.

Study of the equilibrium between copper and dimethylglyoxime in solution, as performed by us using various methods, shows that the copper-dimethylglyoxime system is rather complicated. Several complex compounds which differ in composition, stability, and optical properties are formed in solution depending on conditions.

Solubility of $\text{Cu}(\text{HDm})_2$ in water and in the presence of common ions. The initial $\text{Cu}(\text{HDm})_2$ preparation was obtained from copper sulfate and the disodium salt of dimethylglyoxime, taken in a 1:2 ratio. For this, 0.1 mole of the copper salt, dissolved in 250 ml water, was added in small portions to a solution of disodium dimethylglyoxime (0.2 mole dimethylglyoxime and 0.4 mole NaOH in 200 ml water). In these conditions, i.e., in alkaline media, crystalline copper dimethylglyoxime does not separate, in contrast to nickel dimethylglyoxime, but the solution develops a brown color. By neutralizing the alkali using dilute acid, crystals of $\text{Cu}(\text{HDm})_2$ separate from solution, with a maximum yield on introducing 0.2 g-equivalents of acid.

Analysis of the air-dried precipitate was conducted in the following manner. The quantity of copper was determined by electrolysis after first decomposing the organic portion using ammonium persulfate in presence of sulfuric acid. Dimethylglyoxime held in the $\text{Cu}(\text{HDm})_2$ was precipitated by an excess of a nickel salt as $\text{Ni}(\text{HDm})_2$ at a pH of 5. The $\text{Ni}(\text{HDm})_2$ precipitate was first washed with buffer solution and then with water. The analytical results presented below indicate adequate purity for the preparation:

Found %Cu 21.58; theoretical 21.54; HDm^- 78.4; theoretical 78.36.

In its free state, the $\text{Cu}(\text{HDm})_2$ compound is a black crystalline substance soluble in water, alcohol, acetone, and in other solvents forming reddish-brown solutions. It was first established by its copper content that the water solution became saturated after continuous agitation for a period of 1.5–2 hours. After saturation, the liquid was separated from the solid phase using a pipette with a filtering layer. Copper and dimethylglyoxime content of the water solution were determined by methods described above. Solubility found from copper concentration in the filtrate corresponded to solubility as determined from dimethylglyoxime content and was equal to $6 \cdot 10^{-3}$ mole/liter (at 22°).

Solubility values presented do not agree with literature data. Thus, according to data of V. M. Peshkova [2] the solubility of $\text{Cu}(\text{HDm})_2$ in water at 20° was 1.12% which corresponds to $3.9 \cdot 10^{-2}$ mole/liter. We cannot explain the reason for this large discrepancy (almost 6.5 fold) because V. M. Peshkova did not report methods for determining solubility.

According to conclusions from the solubility product principle, if new chemical compounds do not form on introducing excess copper ions, we should anticipate decreased solubility of the $\text{Cu}(\text{HDm})_2$ precipitate. However, the experiments, a portion of which are presented in Table 1, indicate the complete reverse. Copper sulfate solutions with accurately known concentrations and with a pH not greater than 4 were saturated with copper dimethylglyoxime for a period of 2 hours, after which the total amount of copper in the filtrate was determined. Solubility was calculated from the difference between total and initial copper concentrations.

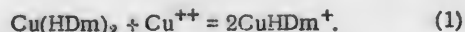
Table 1

Cu(HDm)₂ Solubility in Copper Sulfate Solutions.

Initial copper salt concentration (mole/liter), $C \cdot 10^3$	Total (found) copper salt concentration (mole/liter), $C \cdot 10^3$	Cu(HDm) ₂ solubility (mole/liter), $C \cdot 10^3$
5.0	13.5	8.5
10.0	18.8	8.8
20.0	30.0	10.0
50.0	62.8	12.8
100.0	114.0	14.0
200.0	218.0	18.0

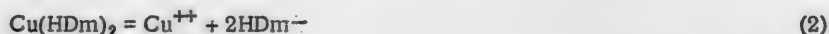
By comparing data of Columns 1 and 3 in Table 1, it can be seen that solubility of Cu(HDm)₂ significantly increases on increasing the concentration of introduced copper salt.

One reason for the precipitate's properties deviating from normal is reaction of the solid phase with copper anions to form ions of the type $PbCl^+$, PbI^+ , HgI^+ , and so on. By analogy, we may assume that the solubility of Cu(HDm)₂ in copper salts is connected with the reaction:



The complex cation CuHDm⁺. The assumption presented above with regard to formation of the complex cation CuHDm⁺ (with excess copper ion) was checked by two methods. Preliminary experiments showed that the optical density of a Cu(HDm)₂ solution was changed

by introducing either an excess of dimethylglyoxime or an excess of copper ion. This change in optical density can be explained by a change in dissociation of the complex in presence of an excess of one of its reactant components:



According to equation (2), introducing excess dimethylglyoxime should have considerably more effect than adding excess Cu⁺⁺ ion. Actually, the exact opposite was observed. We placed 5 ml portions of saturated Cu(HDm)₂ solution in a series of flasks together with 25 ml pH 5 buffer solution (a mixture of sodium acetate and hydrochloric acid) after which increasing quantities of copper sulfate were added to one set of the flasks, and similarly increasing quantities of dimethylglyoxime added to the other. Each solution was brought to a volume of 50 ml and its optical density measured with a 5 cm layer thickness at a 460 mμ wave length (in this spectral region, copper sulfate solution absorbs almost none of the light) (Fig. 2). Measurement results are given in Fig. 1. Quantity (milliliters) of 0.1 molar dimethylglyoxime solution added (curve 1) or copper solution (curve 2) is plotted along the abscissas, and optical density (D) along the ordinate axis.

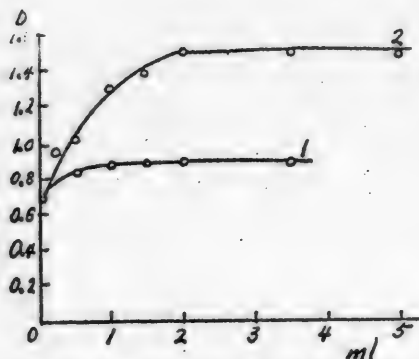


Fig. 1. Change in optical density of Cu(HDm)₂ solution with increasing concentration of both ions.

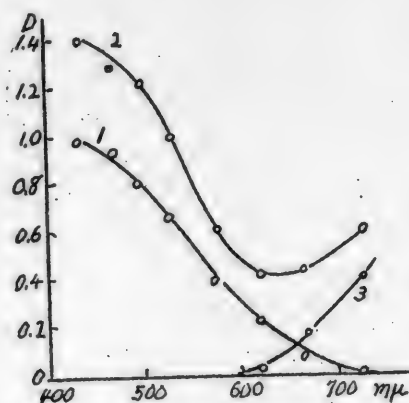


Fig. 2. Absorption spectra of: (1) 0.0006 molar Cu(HDm)₂ solution, (2) 0.0006 M Cu(HDm)₂ solution in presence of 0.01 mole CuSO₄, and (3) 0.01 M CuSO₄ solution.

As can be seen from data of Fig. 1, dimethylglyoxime addition has little effect on optical density of the initial $\text{Cu}(\text{HDm})_2$ solution; on the contrary, addition of copper salt increases the light absorption of the initial solution by almost 1.5 fold. Consequently, in presence of excess copper ion, no change occurs in dissociation equilibrium but rather a chemical reaction takes place to form a new compound (equation 1).

Formation of a complex cation in this condition was also confirmed by observing motion of the colored complex during electrolysis. For these experiments, we used a U-shaped tube with stopcocks. The lower portion of the tube was filled with copper sulfate solution previously saturated with copper dimethylglyoxime, and a copper sulfate solution of the same concentration (side liquid) was placed in the upper portion. The vessel was connected to a direct current source. In a one hour period, the colored layer noticeably moved toward the cathode.

We also studied complex-formation reactions between copper and dimethylglyoxime in solution by methods of physico-chemical analysis. Optical density was taken as a system property. It should, however, be noted that using physico-chemical methods of analysis is somewhat difficult in the given case because the absorption spectra of both compounds — $\text{Cu}(\text{HDm})_2$ and the complex formed with excess copper ion — are rather close (Fig. 2).

Both compounds absorb light rather strongly in the short-wave portion of the spectrum and the difference in their optical properties is of low reliability. In the long-wave region, light absorption for $\text{Cu}(\text{HDm})_2$ is very small, whereas that for the complex formed with excess copper salt is significantly greater; consequently, in this spectrum region, the difference between them should be more clearly expressed. However, copper ions show strong light absorption in the long-wave portion of the spectrum.

Measurements of optical density were also performed in the short-wave and central portions of the spectrum. Results are given below on studying optical properties of an equimolar mixture [3] of copper sulfate and the disodium salt of dimethylglyoxime in a solution buffered at pH 4.5 and constant total volume; 0.1 M solutions were mixed in various ratios so that the total concentration of components (moles/liter) would remain constant. The copper salt concentration decreased in the following manner: $2.4 \cdot 10^{-3}$, $2.2 \cdot 10^{-3}$, $2.0 \cdot 10^{-3}$, and so on. Dimethylglyoxime concentration increased in the same order. Buffer mixture (sodium acetate and hydrochloric acid) was added in the amount of 25 ml per 100 ml total volume, after first neutralizing the disodium salt of dimethylglyoxime with acid. The composition — optical density curves, plotted for comparison in several portions of the spectrum, have the form shown in Fig. 3.

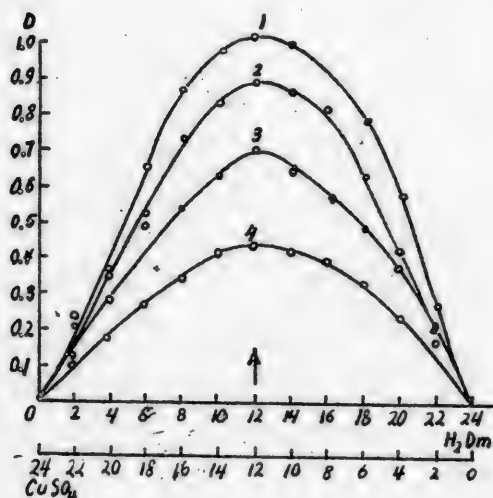


Fig. 3. Composition — optical density curves for the CuSO_4 — H_2Dm system at pH 4.5, layer thickness 5 cm. Wave length (λ) (m μ): 1) 436; 2) 495; 3) 533, 4) 574.

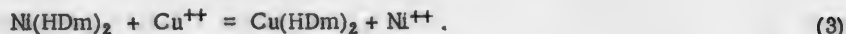
At pH 4.5, maximum light absorption was observed in solutions having components in a 1:1 ratio for all portions of the spectrum. On transition to less acid solutions, the maximum shifts to solutions with larger dimethylglyoxime content. Thus for example at pH 5.5 — 6 the maximum is observed for a mixture with a 5:7 composition (these data are not presented), and at pH 7 — 8 with a 1:2 ratio (Fig. 7). Thus, formation of two compounds in equilibrium with each other takes place in the mentioned conditions. The simpler complex group CuHDm^+ , forms in low concentrations of the coordination ion (in acid media). With increasing pH, concentration of the free anion HDm^- , from the reagent increases and the compound, $\text{Cu}(\text{HDm})_2$, becomes the dominant form in solution. As was shown above, formation of CuHDm^+ is also promoted by introducing excess Cu^{++} ions.

Determining the dissociation constant of CuHDm^+ complex by equilibrium with precipitated $\text{Ni}(\text{HDm})_2$. Solid $\text{Ni}(\text{HDm})_2$ significantly dissolves in presence of a copper salt, although by itself it appears to be one of the most difficultly soluble precipitates. Equilibrium may be attained in a 14 — 16 hour period of continued agitation of the solution. Preliminary experiments also showed that $\text{Ni}(\text{HDm})_2$ solubility in copper salt so-

lutions of constant concentration remained approximately the same over wide pH limits. Consequently, in studying the character of the equilibrium, it was sufficient to follow $\text{Ni}(\text{HDm})_2$ solubility as a function of copper salt concentration. The $\text{Ni}(\text{HDm})_2$ — Cu^{++} system was studied by us only in media having pH below 5, because formation of

basic salts was possible at smaller acidities.

In weakly acid media, dissolving may depend on one of the two reactions:



In connection with the data presented above, however, one should expect that in presence of excess free copper ions equilibrium (4) should have the greater significance (compare column 5 in Table 2). In this case, the principle for determining dissociation constants for the CuHDm^+ complex numerically characterizing the bond energy between the central Cu^{++} atom and the coordinating HDm^- anions, consists in experimentally determining the equilibrium constant for reaction (4):

$$K_{eq} = \frac{[\text{CuHDm}^+]^2 [\text{Ni}^{++}]}{[\text{Cu}^{++}]^2} = \frac{SP_{\text{Ni(HDm)}_2}}{K_{\text{CuHDm}^+}^2} \quad (5)$$

where $SP_{\text{Ni(HDm)}_2}$ is the solubility product for nickel dimethylglyoxime and K_{CuHDm^+} is the dissociation constant for the CuHDm^+ complex.

TABLE 2

Solubility of Precipitated Ni(HDm)_2 in Copper Sulfate Solutions at pH 4.5.

Experiment number	Concentration (g-ions/liter) $\cdot 10^4$				$K_3 \cdot 10^4$	$K_4 \cdot 10^5$
	Initial $[\text{Cu}^{++}]$	$[\text{Ni}^{++}]$ found in filtrate	$[\text{CuHDm}^+]$	$[\text{Cu}^{++}]$ equilibrium.		
1	2	3	4	5	6	7
1	800	30.3	60.7	739.3	1.2	2.0
2	500	22.8	45.6	454.4	1.1	2.2
3	100	6.0	11.9	88.1	0.4	1.1
4	80	4.4	8.9	71.1	0.26	0.7
5	800	30.3	60.7	739.3	1.2	2.0
6	500	21.8	43.6	456.4	1.0	2.0
7	100	5.4	10.7	89.3	0.3	0.8
8	80	4.3	8.6	71.4	0.2	0.6
9	50	3.3	6.7	43.3	0.2	0.8

The working conditions were as follows. Crystalline Ni(HDm)_2 was covered in a flask with copper sulfate solution of known concentration and with buffer mixture having pH 4.5. The flask contents were continually shaken until saturation. Liquid was removed from the residue using a pipette with a filtering layer. Nickel content of the liquid was determined by precipitation with excess dimethylglyoxime with subsequent recrystallization. The CuHDm^+ concentration, forming as a result of reaction, was taken equal to double the nickel concentration, based on equation (4). Equilibrium Cu^{++} ion concentration was found by the difference between initial salt concentration and copper present in the CuHDm^+ . For approximate calculation of equilibrium constants it was assumed that copper sulfate dissociated completely in solution; moreover, we did not consider the effect of buffer mixture anions and other factors having second-order significance. Data of these experiments are presented in Table 2.

Equilibrium constant values for equation (4), calculated from the principle presented, are given in column 7 of Table 2; equilibrium constants calculated assuming that the reaction follows equation (3) are given in column 6. By comparing the data of columns 6 and 7, it can be seen that K_4 changes less than K_3 with change in the copper ion concentration. This confirms correctness of equation selection. Average K_{eq} value for equation (4) was equal to $1 \cdot 10^{-5}$; $SP_{Ni(HDm)_2}$ is $2.2 \cdot 10^{-25}$ [4]. Setting these values into equation (5), we obtain:

$$K_{CuHDm^+} = \sqrt{\frac{2.2 \cdot 10^{-25}}{1 \cdot 10^{-5}}} = 1.5 \cdot 10^{-10}$$

The order of magnitude for the dissociation constant is confirmed by optical investigation data.

Dissociation constant for $CuHDm^+$ complex from studies on optical density as dependent on solution pH.
Copper complex formation with dimethylglyoxime, similar to other complex compounds of metals with weakly acid anions, depends strongly on acidity of the medium. In Fig. 4, is presented a curve for change in optical density of a solution containing $5 \cdot 10^{-4}$ mole/liter $CuSO_4$ and an 8-fold excess of dimethylglyoxime with increasing pH.

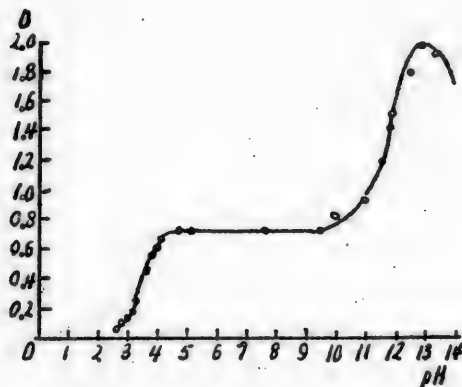
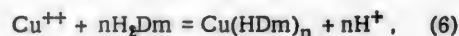


Fig. 4. Change, with pH, of $CuSO_4$ solution optical density in presence of 8-fold dimethylglyoxime excess.

Light absorption sharply increases over pH limits from 2.8 to 4.5 and then remains constant for pH from 4.5 to 9. With further pH increase, absorption again increases. A curve of this shape is characteristic of stepwise complex formation. The second stage is limited by the region in which alkali decomposes the complex (discussed in detail below).

Abrupt increase in the optical density curve between pH 2.8 to 4.5 may be attributed to formation of either complex: $CuHDm^+$ or $Cu(HDm)_2$. If the reaction taking place here may be expressed by the scheme:



then, from the equation for equilibrium constant:

$$K_{eq} = \frac{[Cu(HDm)_n] [H^+]^n}{[Cu^{++}] [H_2Dm]^n} \quad (7)$$

after taking logarithms and rearranging, we obtain the equation:

$$-n \log [H^+] = -\log K_{eq} \cdot [H_2Dm]^n + \log \frac{[Cu(HDm)_n]}{[Cu^{++}]} \quad (8)$$

We took a large excess of dimethylglyoxime in a series of solutions so that the $[H_2Dm]$ value could be taken as constant. The first term of the right side of the equation then likewise becomes constant (A), and the relationship between the variables can be expressed by the linear equation:

$$n \text{ pH} = A + \log \frac{[Cu(HDm)_n]}{[Cu^{++}]} \quad (9)$$

where n — is the slope ($\tan \alpha$), numerically equal to the quantity of HDm^- coordination ions. Thus, if solution pH is known, the problem reduces to experimentally determining $Cu(HDm)_n$ complex concentration. In Table 3 optical densities are given for a solution containing $5 \cdot 10^{-4}$ moles/liter $CuSO_4$ and $40 \cdot 10^{-4}$ moles/liter dimethylglyoxime at various pH.

TABLE 3

Optical Density of a $5 \cdot 10^{-4}$ Molar CuSO_4 Solution (in Presence of 8-fold Excess Dimethylglyoxime) as Dependent on pH. Absorption Layer Thickness 5 cm.

Experiment Number	$[\text{H}^+]$ (ions/liter) $\cdot 10^4$	pH	Optical density \bar{D} at $\lambda = 436 \text{ m } \mu$	Concentration (moles/liter) $\cdot 10^4$			$\log \frac{\text{Cu(HDm)}_n}{[\text{Cu}^+]} + 1 \cdot K_{\text{eq}} \cdot 10^5$	
	$[\text{Cu(HDm)}_n]$			$[\text{Cu}^{++}]$	$[\text{H}_2\text{Dm}]$			
1	2	3	4	5	6	7	8	9
1	25	2.6	0.07	0.5	4.5	39.5	0.0457	0.7
2	19.9	2.7	0.09	0.6	4.4	39.4	0.1347	0.7
3	7.9	3.1	0.17	1.2	3.8	38.8	0.4994	0.6
4	5.0	3.3	0.25	1.7	3.3	38.3	0.7119	0.7
5	3.2	3.5	0.36	2.5	2.5	37.5	1.0000	0.9
6	2.5	3.6	0.46	3.2	1.8	36.8	1.2499	1.2
7	1.6	3.8	0.55	3.8	1.2	36.2	1.5006	1.4
8	1.0	4.0	0.60	4.2	0.8	35.8	1.7202	1.5
9	0.6	4.2	0.67	4.7	0.3	35.3	—	—
10	0.3	4.5	0.72	5.0	0	35.0	—	—
11	0.06	5.2	0.72	5.0	0	35.0	—	—

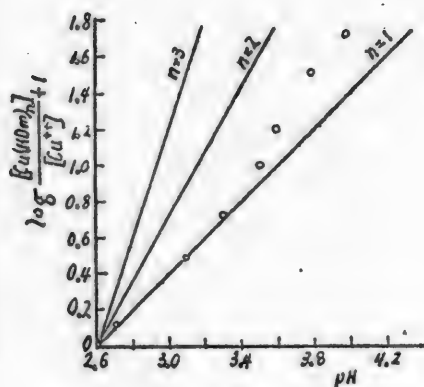


Fig. 5. Change in $\log \frac{[\text{Cu(HDm)}_n]}{[\text{Cu}^{++}]} + 1$ as dependent on pH.

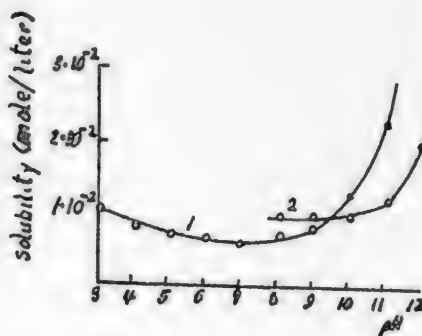
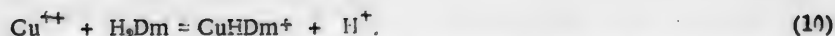


Fig. 6. Cu(HDm)_2 solubility in buffered solutions. Curve 1) solubility in acetate solution; Curve 2) solubility in borate solution.

It can be seen from the Table 3 and Fig. 4 data that copper ions are almost completely tied up in the Cu(HDm)_n complex beginning with pH 4.8. The optical density of such a solution was equal to 0.72. Consequently, we may calculate the Cu(HDm)_2 concentration in other solutions from their optical density. The equilibrium Cu^{++} ion concentration is equal to the difference between the initial total

Cu^{++} concentration and the copper tied up in the complex. Fig. 5 was plotted based on the data of Table 3 and reflects equation (9), i.e., the dependence of $\log \frac{[\text{Cu(HDm)}_n]}{[\text{Cu}^{++}]} + 1$ (ordinate axis) to pH (abscissas axis); both variables are plotted to the same scale here. The straight lines show relationships calculated assuming that $n = 1$, $n = 2$, and $n = 3$; the points correspond to the experimental results.

Over pH limits from 2.6 to 3.6, experimental data are close to the line with $n = 1$; it follows from this that the number of coordinating HDm^- ions is likewise equal to unity, i.e., in acid media the complex CuHDm^+ forms to the largest extent, according to the equation:



With further increase in pH the slope increases, evidently in consequence of forming significant quantities of the complex $\text{Cu}(\text{HDM})_2$.

Data of Table 5 were also used for calculating dissociation constants for the CuHDM^+ complex by a relationship derived from equation (10):

$$K_{\text{eq}} = \frac{[\text{CuHDM}^+][\text{H}^+]}{[\text{Cu}^{++}][\text{H}_2\text{Dm}]} = \frac{K_{\text{H}_2\text{Dm}}}{K_{\text{CuHDM}^+}} \quad (11)$$

from which:

$$K_{\text{CuHDM}^+} = \frac{K_{\text{H}_2\text{Dm}}}{K_{\text{eq}}} \quad (12)$$

where $K_{\text{H}_2\text{Dm}}$ is the first dissociation constant for dimethylglyoxime, numerically equal to $8 \cdot 10^{-12}$ [5]. The equilibrium constant, based on a large number of experiments, only a portion of which are presented in Table 5*, was approximately equal to $1 \cdot 10^{-1}$. Consequently $K_{\text{CuHDM}^+} = 0.8 \cdot 10^{-11}$; this is close to the numerical value for the constant as found by entirely different procedures, namely by equilibrium with precipitated $\text{Ni}(\text{HDM})_2$ (see above).

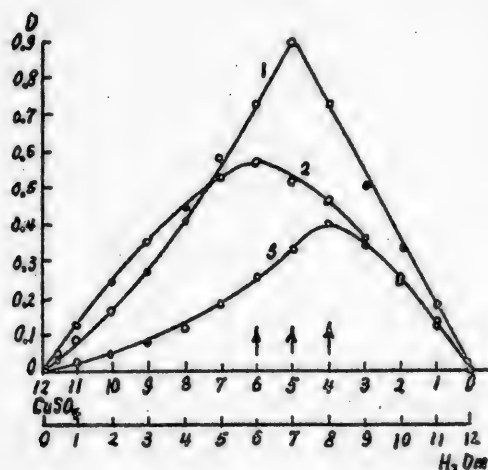


Fig. 7. Optical properties of equimolar mixtures of CuSO_4 and H_2Dm in neutral and alkaline media. pH: 1) 12.3, 2) 9-10, 3) 7-8.

concentration varied from 1.2 moles/liter to zero and dimethylglyoxime concentration from zero to 1.2 moles/liter. In addition, to hold in solution copper hydroxide which does not react with dimethylglyoxime, we added a third component: 5 ml 0.1 M sodium pyrophosphate solution mixed with hydrochloric acid, to the weakly alkaline solutions, and 1 ml of 0.5 M sodium tartrate to the strongly alkaline ones. Uniform pH was obtained by adding buffer mixture (phosphate or borate) in a quantity equal to half the total volume. Optical density was measured with a 5 cm layer thickness and with a 495 mμ wave length (Fig. 7).

As may be seen from Fig. 7, at pH 7-8 maximum optical density is observed for a solution with a 1:2 composition; i.e., at this acidity the stable compound is $\text{Cu}(\text{HDM})_2$. On transition to more alkaline solutions, the height of the maximum increases and it also changes its location with regard to pH; this indicates formation of new strongly colored compounds. Thus, at pH about 10, maximum light absorption shifts in the direction of a solution with a 1:1 ratio, and then at pH equal approximately to 12, it again returns to solutions with larger dimethylglyoxime contents.

According to data from composition studies, the alkaline medium transformations may be described in the following manner. Replacement of the second hydrogen ion of dimethylglyoxime by copper ions is facilitated

* No Table 5 appears in the original. Publisher.

Copper complexes with dimethylglyoxime in alkaline media.

The $\text{Cu}(\text{HDM})_2$ complex is soluble in alkalis — NaOH and KOH — with formation of greenish-brown solutions. On neutralizing the alkaline solutions, $\text{Cu}(\text{HDM})_2$ again crystallizes. Increase in solubility with increasing solution pH is shown in Fig. 6.

The solubility changes slightly over rather wide pH limits (from 4 to 9). At pH above 9 it significantly increases. It is characteristic that the solubility curve increase is located at the very same pH limits at which optical density increases (Fig. 4).

$\text{Cu}(\text{HDM})_2$ was observed to be similar to the dioximes $\text{Pd}(\text{HDM})_2$ and $\text{Pt}(\text{HDM})_2$, both of which likewise are readily soluble in alkalis. L.A. Chugaev, [1] claimed that reaction with alkalis indicated acid properties in the dioximes, implying by this, evidently, the tendency to replace two hydrogen atoms remaining in the oxime groups. To the present time, however, it has not been possible to determine the composition of products formed in alkali and to explain the reaction chemistry. In connection with this, it was of interest to study in detail the ratio of $\text{Cu}(\text{HDM})_2$ to alkali. The optical method was taken as the basis of study.

In studying copper compound compositions in alkaline media, we prepared a series of equimolar solutions in which copper salt c

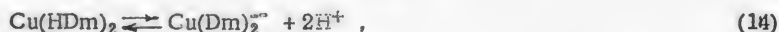
TABLE 4

Optical Density of Mixtures of CuSO_4 Solutions with Dimethylglyoxime in Alkaline Media at Varying pH.
 CuSO_4 concentration = $2.5 \cdot 10^{-4}$ moles/liter, dimethylglyoxime concentration = $40 \cdot 10^{-4}$ moles/liter.
 Absorption layer thickness 5 cm.

Experiment number	pH	Optical density D		Concentration (moles /liter)		$\log \frac{[\text{Cu}(\text{Dm})_n]}{[\text{Cu}(\text{HDm})_2]} + 2$
		at	at	$C \cdot 10^5$		
		$\lambda = 436 \text{ m}\mu$	$\lambda = 465 \text{ m}\mu$	$\text{Cu}(\text{HDm})_2$	$\text{Cu}(\text{Dm})_n$	
1	2	3	4	5	6	7
1	7.7	0.36	0.33	25	0	—
2	9.5	0.36	0.33	25	0	—
3	10.5	0.41	0.35	23.6	1.4	0.7732
4	10.75	0.43	0.36	23.0	2.0	0.9393
5	11.0	0.45	0.37	22.4	2.6	1.0647
6	11.25	0.50	0.39	20.5	4.5	1.3415
7	11.5	0.59	0.41	15.8	9.2	1.7651
8	11.75	0.69	0.45	11.9	13.1	2.0417
9	12.00	0.75	0.46	8.5	16.5	2.2881
10	12.25	0.78	0.48	7.9	17.1	2.3354
11	12.5	0.90	0.55	5.0	20.0	2.6021
12	12.75	1.02	0.58	—	—	—
13	12.9	1.0	0.54	—	—	—
14	13.0	0.95	0.50	—	—	—

in alkaline media. As a result of this, compounds of the disubstituted salt type are formed: CuDm or $\text{Cu}(\text{Dm})_2^{--}$. Formation of complex anions in alkaline media is confirmed, particularly, by observing solution behavior on electrolysis.

Further, we present results of studying portions of the optical density curves at pH 10–12 (Fig. 4). Under these conditions the following equilibria are possible, shifting to one or the other side depending on pH of the medium:



In the event compounds with a 1:1 ratio are formed [equations (13) or (15)], the latter reaction [equation (15) is the more probable], because according to the first acid dissociation constant for dimethylglyoxime (see above) at pH up to 12, dimethylglyoxime is mainly found in the H_2Dm or HDm^- form. For characteristics of equilibrium with significant or constant excess dimethylglyoxime, it is necessary to determine the relationship:

$$\frac{[\text{Cu}(\text{Dm})_n]}{[\text{Cu}(\text{HDm})_2]} = f[\text{H}^+]. \quad (16)$$

Evidently, in the event of reaction by equations (13) or (14), the ratio, $\frac{[\text{Cu}(\text{Dm})_n]}{[\text{Cu}(\text{HDm})_2]}$, will vary with the square of hydrogen ion concentration ($n = 2$), and in event reaction is by equation (15) this ratio will depend on hydrogen ion concentration to the first degree ($n = 1$).

For finding concentration of $\text{Cu}(\text{HDm})_2$ or of compounds corresponding to disubstituted salt formulas, namely CuDm or $\text{Cu}(\text{Dm})_2^{--}$, we may use a system of equations for mixtures of two colored components.

$$D_{\lambda_1} = (E_{\lambda_1}^I C' + E_{\lambda_1}^{II} C'') d, \quad (17)$$

$$D_{\lambda_2} = (E_{\lambda_2}^I C' + E_{\lambda_2}^{II} C'') d, \quad (18)$$

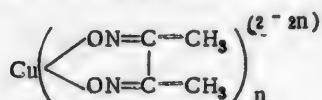
where D_{λ_1} is the optical density of the solution at a wave length λ_1 ; D_{λ_2} is optical density at wave length λ_2 ; $E_{\lambda_1}^I$ and $E_{\lambda_2}^I$ are molar extinction coefficients for one compound; $E_{\lambda_1}^{II}$ and $E_{\lambda_2}^{II}$ are analogous values for the second compound; C' and C'' are component concentrations; and d is layer thickness.

A series of solutions was prepared containing $2.5 \cdot 10^{-4}$ moles/liter CuSO_4 and $40 \cdot 10^{-4}$ moles/liter dimethylglyoxime with varying pH. As buffer we used a mixture of borax and caustic to the extent of 75 ml per 100 ml total volume. Optical density was measured with a 5 cm layer thickness in two portions of the spectrum—at 436 m μ and at 465 m μ . In calculating molar extinction coefficients by the formula $\log I_0/I = Ecd$ we used for $\text{Cu}(\text{HDM})_2$ the optical density of solutions which did not change over the pH limits from 7.7 to 9.5, and for the assumed compounds CuDm or $\text{Cu}(\text{Dm})_2^{--}$ the maximum optical density in alkaline media corresponding to solution 12 (Table 4). E_{436} and E_{465} for $\text{Cu}(\text{HDM})_2$ were equal, respectively, to 290 and 260; analogous values for $\text{Cu}(\text{Dm})_n$ were equal to 800 and 460. In Table 4, optical densities are given for the solutions and calculations made based on this residual value.

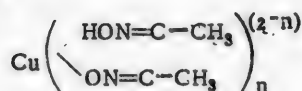
Fig. 8 was based on data of Table 4; from it we can see that the experimental points are close to the line having slope $n = 1$.

Thus, in accordance with the previously presented discussion, $n = 1$ and reaction at pH 10-12 goes by equation (15). These results are in agreement with earlier data on composition by methods of physico-chemical analysis.

Complexes of the disubstituted salt type, CuDm or $\text{Cu}(\text{Dm})_2^{--}$, should be more stable as compared with complexes of the acid salt type, CuHDM^+ or $\text{Cu}(\text{HDM})_2$. This should be expected based on comparing structural characteristics of compounds of the named type.



and



(it is, moreover, possible in compounds of the acid salt type to have coordination bonds between copper and the second oxime group). Greater stability should be expected for the neutral salt type compounds by analogy with a similar phenomena in the case of certain complex compounds of metals with hydroxy acids, diphenylthiocarbazone, and others.

To confirm the conclusions presented above and also to characterize the compounds formed in a given system in an alkaline media, it was of interest to compare the stability of the named compound groups. Determining numerical values for the decomposition constant is extremely difficult because there are no standards characteristic of other copper complexes stable in alkaline media. However, a number of qualitative observations confirm the significant difference in stability of copper dioxime complexes formed in weakly acid and in alkaline media. This is clearly shown by the behavior of copper dioxime with certain reagents in various media. Particularly, by the characteristic behavior with hydroxyacid anions—such as tartaric and citric—with which copper forms complex compounds stable over the same limits as the copper dioximes. Experiments were set up in the following manner. 1 ml of a 0.1 M CuSO_4 solution was placed in a flask, a four-fold excess of dimethylglyoxime added as well as the same quantity of a tartaric acid salt. The contents of the flask were diluted to 50 ml by a buffer solution with known pH. Along with this, for comparison of the color, we prepared buffer solutions containing only the copper salt and dimethylglyoxime, as well as solutions containing only the copper salt and tartaric acid. It was found that weakly acid solutions containing copper, dimethylglyoxime, and tartaric acid turned a green color which was characteristic of tartaric acid copper complex—the more stable copper tartrate complex. And, on the contrary, alkaline solutions developed a reddish-brown color, characteristic of copper dioximes. The reddish-brown color did not change with high pH values even in presence of 50-fold excess of tartrate—the copper dioxime is the more stable. The same thing was observed on introducing citrates; however, significantly less of the latter is required for decomposing copper dioxime. As another example to confirm increased bond stability in copper dioximes formed in alkaline media, we note the behavior of $\text{Cu}(\text{HDM})_2$ and ammonia. Ammonia alone does not decompose copper dioxime completely (alkaline medium). If, however, solution pH is decreased by addition of ammonium chloride, then complete decomposition of the copper dioxime takes place immediately.

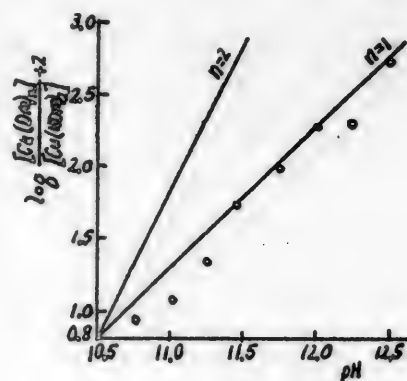


Fig. 8. Optical density of CuSO_4 —dimethylglyoxime solution at varying pH in alkaline medium.

SUMMARY

1. The reaction of complex formation between copper and dimethylglyoxime was studied at varying solution acidities.

2. It was shown that in weakly acid media and also in presence of excess Cu^{++} ions, a compound having the composition CuHDM^+ is formed in addition to the known compound $\text{Cu}(\text{HDM})_2$. This follows from the increased solubility of $\text{Cu}(\text{HDM})_2$ in presence of copper salts, physico-chemical investigation of the compound composition in solution, and also by observing the motion of the colored solution layer during electrolysis:

3. The dissociation constant $K = \frac{[\text{Cu}^{++}][\text{HDM}^-]}{[\text{CuHDM}^+]}$ for the CuHDM^+ complex was determined by two methods: via solubility of $\text{Ni}(\text{HDM})_2$ in copper salts ($1.5 \cdot 10^{-10}$) and via an optical method ($0.8 \cdot 10^{-20}$).

4. It was shown that the solubility of $\text{Cu}(\text{HDM})_2$ in alkalies is connected with formation of new intensively colored compounds, probably having the compositions: CuDm and $\text{Cu}(\text{Dm})_2^-$.

5. The behavior of $\text{Cu}(\text{HDM})_2$ with ammonia, tartrates, and citrates was studied, and it was shown that the change in composition in alkaline media is accompanied by increase in stability of the copper dioxime complexes.

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Received March 28, 1953.

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SOLUBILITY AND ADSORPTION OF AROMATIC ACIDS AS DEPENDENT ON NATURE AND POSITION OF SUBSTITUTENT GROUPS

N. F. Ermolenko and N. L. Lemets

Establishment of a relation between adsorption of organic acids and polarity of mixed media has been the subject of a large number of papers [1]. However, there are only a few studies in which the effect of structural characteristics of the organic acids on their solubility and adsorption was considered, [2].

Since it was shown that not only the polarity of the medium, but also the constitutional characteristics of the adsorbed molecules had an effect on the solubility and adsorption of organic acids, the problem was set in the present study to investigate the effect of nature and position of substituents in organic acids with regard to their adsorption on charcoal from solution in mixed organic media.

It was important, on the one hand, to establish the relationship between adsorption and solubility for these acids as dependent on their constitutional characteristics. On the other hand, it was necessary to explore the relationship between behavior of these acids in solution and the mixed medium's polarity, particularly its dielectric polarization.

It should not be expected that differences in location of the same substituent group in the molecules of organic acids will affect solubility and adsorption of the acids to the same degree as differences in substituent group in the same location; both factors affect the polarity of the molecule as a whole; Different substituent groups, although they may occupy the same location in the molecule, can affect organic acid solubility and adsorption values to a significant degree by virtue both of differences in the moments of these groups as well as of differences in their tendency to form hydrogen bonds.

In the present study we took as the adsorbed organic acids: o-, m-, and p-nitrobenzoic, o- and p-chlorobenzoic, and p-hydroxybenzoic acids. All the acids were first carefully purified.

As mixed media we employed: $C_6H_6-CCl_4$; $C_6H_6-CHCl_3$; $C_6H_6-C_2H_5OH$; $C_6H_6-(CH_3)_2CO$; CCl_4-CHCl_3 ; $CCl_4-C_2H_5OH$; $CCl_4-C_6H_5NO_2$; $(CH_3)_2CO-C_2H_5OH$; $CHCl_3-C_2H_5OH$; $(CH_3)_2CO-C_6H_5NO_2$.

The solvents were likewise carefully purified; purity was checked by their constants. Ash-free activated wood charcoal was used as an adsorbent.

Among the constitutional characteristics studied were the effect of the nature of the substituent and its location in the o- and p-positions in benzoic acid molecules with regard to solubility and adsorption.

Moreover, we studied the effect of substituent location in nitrobenzoic acids on adsorption and solubility. In all cases mixed media were used.

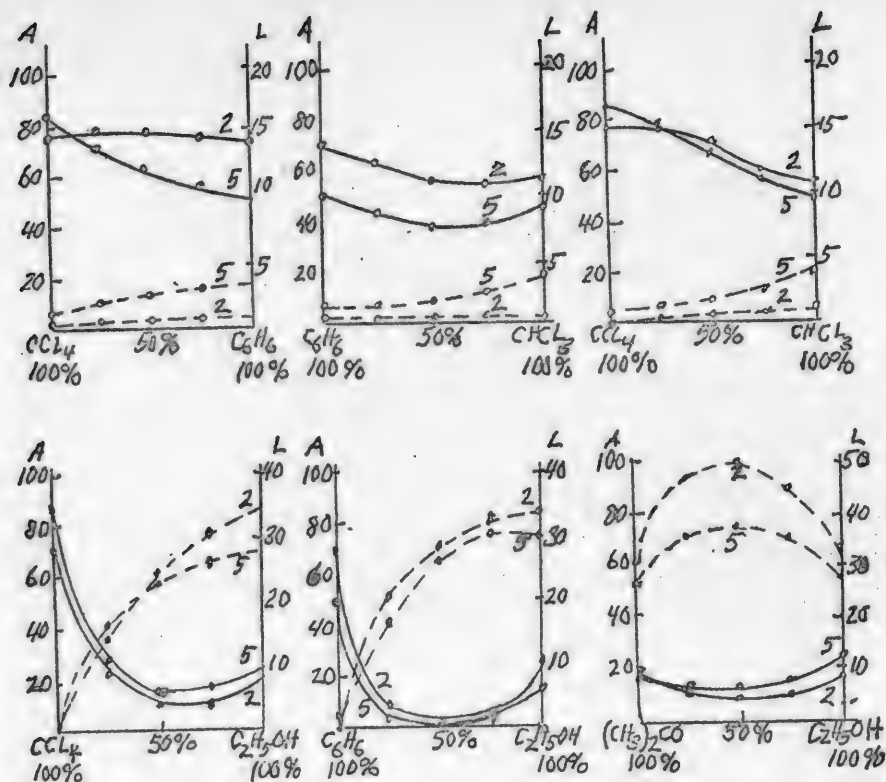
DISCUSSION OF RESULTS

1. Behavior of o-substituted benzoic acid in mixed media. Figures 1-6 present data on adsorption and solubility of o-chlorobenzoic and o-nitrobenzoic acids when using a number of mixed media.

o-Nitrobenzoic and o-chlorobenzoic acids appear significantly similar in their behavior in the $C_6H_6-CCl_4$, $C_6H_6-CHCl_3$, and CCl_4-CHCl_3 media. In all cases we observed complete correspondence between solubility and adsorption (Figs. 1-3). The similar relationship is connected with solvation of the acid by molecules of the mixed media.

With higher solubility of o-chlorobenzoic acid, which is connected with greater solvation by molecules of the medium, we observed smaller adsorption on charcoal. o-Chlorobenzoic acid, with a less polar functional group $-Cl$ ($\mu = 1.56 \cdot 10^{-18}$)—as compared with o-nitrobenzoic acid, which has the more polar nitro group ($\mu = 3.8 \cdot 10^{-18}$), is more solvated by molecules of the non-polar C_6H_6 and CCl_4 and consequently, the first acid's solubility is greater than that of the second, while their adsorbabilities are in the reverse ratio.

On transition to media with more polar components ($CHCl_3$) in the mixture, the solubility of o-chlorobenzoic



Figs. 1-6. Solubility (L) (dashed line) and adsorption (A) (solid line) for *o*-substituted benzoic acids in mixed media. 2) *o*-Nitrobenzoic acid; 5) *o*-chlorobenzoic acid.

acid increases more sharply than that of *o*-nitrobenzoic acid, in view of the fact that the first is solvated better by chloroform than the second (Figs. 2 and 3).

In mixed media in which one component is strongly polar (C_2H_5OH), the more polar *o*-nitrobenzoic acid is solvated better and therefore is more soluble than is the *o*-chlorobenzoic acid.

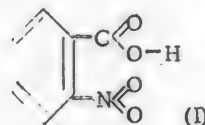
This difference exists more clearly as the solubility-composition curves approach the polar component and amounts to 4.7 g/100 ml in pure alcohol.

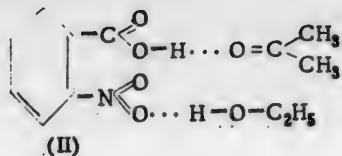
In pure benzene (Fig. 5) the less polar *o*-chlorobenzoic acid has greater solubility than the more polar *o*-nitrobenzoic acid by 1.24 g/100 ml, and its adsorption is less by 20.36%. On transition to alcohol the relation is changed in view of better solvation of the more polar *o*-nitrobenzoic acid by the polar component of the medium.

In view of the same structure and similar composition for the two *o*-substituted benzoic acids, the shapes of the solubility and adsorption curves for both acids are very similar to one another in the same mixed solvent. In a mixture of two polar solvents (Fig. 6) the mentioned acids behave similarly in solubility and adsorption. They differ only in a quantitative manner: the solubility of the more polar *o*-nitrobenzoic acid in a $(CH_3)_2CO-C_2H_5OH$ mixture is greater than that of the less polar *o*-chlorobenzoic acid by 5.7 g/100 ml in pure alcohol, by 3.6 g/100 ml in pure acetone, and by 12.4 g/100 ml in a 1:1 mixture of these materials.

For acids which contain a nitro or other group which can form hydrogen bonds in the *o*-position to the carboxyl group, it is possible to form the internal complex (I) in nonpolar media. This phenomenon is known as the "o-effect".

The significant increase in solubility of *o*-nitrobenzoic acid in a mixture of two polar components, $(CH_3)_2CO-C_2H_5OH$, with a 1:1 ratio of the latter, indicates possible formation of a more complicated acid-alcohol-acetone complex (II).

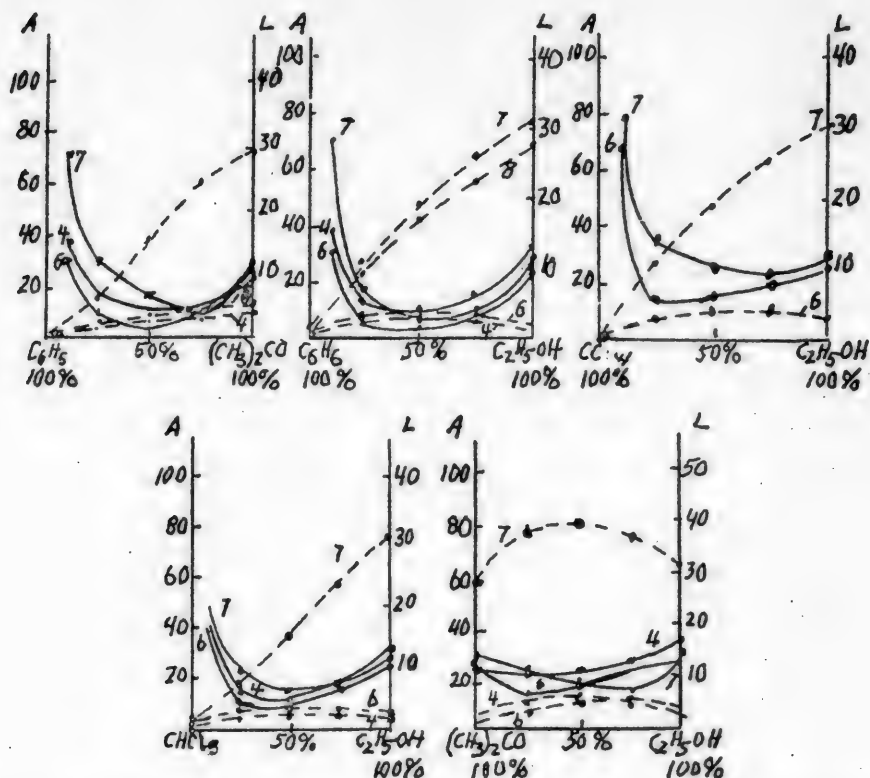




Maximum solvation (or solubility) of o-nitrobenzoic acid and o-chlorobenzoic acids in the indicated mixed medium, naturally corresponds to minimum adsorption; therefore, adsorption of the acids from mixed solvents passes through a minimum from pure acetone to pure alcohol, and the solubility through a maximum.

The differences observed in absolute solubility and adsorption values of the mentioned acids in the same media are caused by differences in absolute values for substituent group polarities.

2. Behavior of p-substituted benzoic acid in mixed media. p-Substituted benzoic acid is very weakly solvated by nonpolar media (C_6H_6 , CCl_4), as compared to benzoic acid. Consequently, it is poorly soluble in these media: solubility of p-nitrobenzoic acid amounts to 0.084 g/100 ml in C_6H_6 and 0.021 g/100 ml in CCl_4 ; that of p-chlorobenzoic acid is 0.118 g/100 ml in C_6H_6 and 0.059 g/100 ml in CCl_4 ; and finally, that of p-hydroxybenzoic acid is 0.52 g/100 ml in C_6H_6 and 0.435 g/100 ml in CCl_4 .

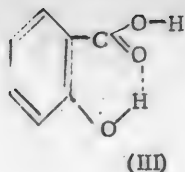


Figs. 7-11. Solubility (L) (dashed line) and adsorption (A) (solid line) for p-substituted benzoic acids in mixed media. Solubility data for o-hydroxybenzoic acid are given for comparison (Fig. 8). 4) p-Nitrobenzoic acid; 6) p-chlorobenzoic acid; 7) p-hydroxybenzoic acid; 8) o-hydroxybenzoic acid.

However, although the solubility of p-chlorobenzoic and p-nitrobenzoic acids does not increase significantly with increase in the polar component in mixed $C_6H_6-(CH_3)_2CO$ and $CCl_4-C_2H_5OH$ media, the solubility of p-hydroxybenzoic acid sharply increases with increase in polar component concentration in the medium.

This may be connected with the better conditions for forming hydrogen bonds between the medium's polar component and the $COOH$ and OH groups of the hydroxybenzoic acid, (Figs. 7, 8, 9).

o-Hydroxybenzoic or salicylic acid is less soluble in the corresponding mixed medium ($C_6H_6-C_2H_5OH$) than p-hydroxybenzoic acid (Fig. 8); this may be related to the appearance in salicylic acid of cyclization or the o-effect (III) [3].



In all systems in which the medium was a mixture of a nonpolar or weakly polar component with a polar one (Figs. 7-9), the solubility of the *p*-benzoic acid derivative taken by us increased with increase in polar component content in the mixed medium or with increase in its dielectric polarization ($P_{1,2}$)*.

In *p*-nitro and *p*-chlorobenzoic acids, the substituent functional group does not contain hydrogen able to form hydrogen bonds; consequently, if the polar component of the mixed medium likewise does not contain such hydrogen [(CH₃)₂CO], then solvation of such groups will be a minimum; this will result in low solubility of these acids in the stated media.

However, for *p*-nitrobenzoic acid in the C₂H₅OH-C₂H₅OH system, formation of hydrogen bonds between the C₂H₅OH molecule and the $\text{—N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ group (or its solvation) hinders dimerization of the alcohol; as is known, the bond energy for alcohol dimer formation is 6.2 kcal/mole, whereas that for water is 4.5 kcal/mole. This naturally does not exclude the possibility [4] of dimerizing the alcohol molecules and other dipolar molecules by simple interaction of the dipoles.

Adsorption of *p*-substituted benzoic acids goes through a minimum with change in the ratio of the polar or weakly polar to the nonpolar component in the mixed medium (Figs. 7-10). In all cases, adsorption of these acids fell sharply on transition from a nonpolar to a polar solvent. Location of the minimum varies somewhat with the nature of the substituent group.

The location of the minimum for adsorption of *p*-hydroxybenzoic acid, which was more soluble in a mixed medium with a predominately polar component, corresponded to 65-75% content of the polar component in the mixture; the adsorption minimum for *p*-nitro- and *p*-chlorobenzoic acids corresponded to a 35-50% content of the polar component in the mixture.

Passage of adsorption through a minimum for mixed media may be explained by several factors. If the fundamental factor is taken as solvation, then one must assume in this case either the action of double solvation (polar and nonpolar portions of the molecule by corresponding components of the medium) or an association of the molecules of the polar component which increases its moment.

The location of the adsorption minimum corresponding to the maximum on the curves for change in dielectric polarization of the polar component in the mixture (P_2), is determined to a large degree by the degree of solvation of the molecules being adsorbed.

Behavior of *p*-substituted benzoic acids in a mixed medium of two polar components [(CH₃)₂CO-C₂H₅OH] differs from its behavior in the systems discussed (Fig. 11).

Here the *p*-hydroxybenzoic acid is more soluble than the other two acids; its excess solubility corresponds to 27-28 g/100 cm³ in pure alcohol, 26-27 g/100 cm³ in pure acetone, and 34-35 g/100 cm³ in their 1:1 mixture.

The solubility of *p*-hydroxybenzoic acid in a mixed medium of two polar components passes through a maximum; the adsorption passes through a minimum; this is likewise associated with optimum solvation of the acid molecules at a molar ratio rather close to 1:1 for the two polar components of the mixed medium.

In the behavior of *p*-chloro and *p*-nitrobenzoic acids, the factor of low total polarity of the acid molecule (in the sense of electrostatic reaction of the dipoles and the small possibility of forming hydrogen bonds with the molecules of the medium) leads to the condition that the solubility and the adsorption both change slightly with change in the polar component ratio in the medium.

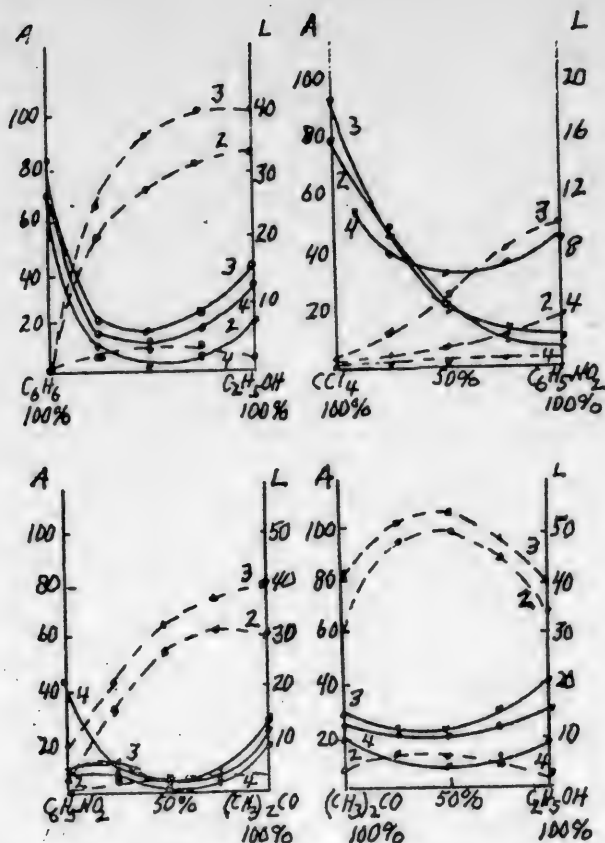
3. Effect of substituent position in benzoic acid on its solubility and adsorption. The position of the same

* The dielectric polarization value for a mixed medium is obtained, as we know, starting from the Mosotti equation:

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon - 2} \frac{C_1 M_1 + C_2 M_2}{d_{1,2}} = C_1 P_1 + C_2 P_2,$$

where $P_{1,2}$ is the dielectric polarization of the mixture, ϵ is the dielectric constant of the mixture, M_1 and M_2 are the molecular weights of the components of the mixed medium, C_1 and C_2 are the mole fractions of the components, $d_{1,2}$ is the density of the medium, and P_1 and P_2 are the dielectric polarizations for the components.

The value of the dielectric polarization of a polar component with a nonpolar second component, in terms of P_1 , is $P_2 = \frac{P_{1,2} - C_1 P_1}{C_2}$.



Figs. 12-15. Effect of nitro-group position in nitrobenzoic acids on solubility (L) (dashed line) and adsorption (A) (solid line) in mixed media.

2) o-Nitrobenzoic acid; 3) m-nitrobenzoic acid; 4) p-nitrobenzoic acid.

alcohol dipole on dimerization evidently becomes stronger [5] (Fig. 12).

In the $\text{CCl}_4\text{-C}_6\text{H}_5\text{NO}_2$ system, the change in adsorption is inverse to the change of solubility, i.e., the more the solubility of a nitrobenzoic acid falls, the more its adsorption increases (Fig. 13). Similar changes in solubility and adsorption of o-, m-, and p-nitrobenzoic acids were observed also with change in component ratio of mixtures in the $\text{C}_6\text{H}_5\text{NO}_2\text{-(CH}_3)_2\text{CO}$ system (Fig. 14).

In mixed media of two polar components (Fig. 15), the solubility of all three nitrobenzoic acids passes through a clearly expressed maximum at a 1:1 ratio of $(\text{CH}_3)_2\text{CO}$ to $\text{C}_2\text{H}_5\text{OH}$ in the mixture. A particularly sharp solubility maximum is shown by the more soluble, and consequently more solvated, o- and m- acids. Evidently, for them it is more characteristic to form hydrogen bonds both with alcohol molecules and with acetone, as was shown above.

Adsorption of all three nitrobenzoic acids passes through a minimum, lying at the same component ratio in the medium; this confirms our suppositions with regard to the role of solvation in the processes of solution and adsorption of acids.

SUMMARY

The relationship of solubility and adsorption was studied for benzoic acid derivatives as dependent on the nature and location of the substituent, as well as the polarity of the mixed media.

1. It was shown that an inverse relationship exists between adsorption of o-, m-, and p-substituted benzoic acids on charcoal from solutions in mixed organic media and their solubility. If the adsorption curve passes through a maximum, the solubility curve passes through a minimum.

substituent in a benzoic acid derivative changes the molecule polarity and consequently should affect its solubility and behavior in solution.

In this case we studied solubility and adsorption of o-, m-, and p-nitrobenzoic acid in the mixed media: $\text{C}_6\text{H}_6\text{-C}_2\text{H}_5\text{OH}$, $\text{CCl}_4\text{-C}_6\text{H}_5\text{NO}_2$, $(\text{CH}_3)_2\text{CO-C}_2\text{H}_5\text{OH}$, and $(\text{CH}_3)_2\text{CO-C}_6\text{H}_5\text{NO}_2$.

In view of the vanishingly small solubility of p-nitrobenzoic acid in CCl_4 it was only possible to study its behavior in mixtures of two polar or one polar and nonpolar component, (Figs. 12-15).

A general characteristic of p-nitrobenzoic acid is its lower solubility both in nonpolar and in polar media. Consequently, the solubility of p-nitrobenzoic acid changes only slightly, passing through a small maximum in traversing certain systems [$\text{C}_6\text{H}_6\text{-C}_2\text{H}_5\text{OH}$ and $(\text{CH}_3)_2\text{CO-C}_2\text{H}_5\text{OH}$]. Solubilities of o- and m-nitrobenzoic acids sharply increase with transition through mixed media ($\text{C}_6\text{H}_6\text{-C}_2\text{H}_5\text{OH}$, $\text{CCl}_4\text{-C}_6\text{H}_5\text{NO}_2$; Figs. 12 and 13) from the nonpolar component to the polar one; this indicates increased solvation of the acid in the more polar medium. In the direction of the more polar component, dielectric polarization of the mixture ($P_{1,2}$) also increases.

In the mixed medium $\text{C}_6\text{H}_6\text{-C}_2\text{H}_5\text{OH}$, adsorption of o-, m-, and p-nitrobenzoic acids passes through a minimum lying in a region corresponding to a 1:1 component ratio in the medium, and corresponding to the highest conditions of acid solvation, because the ethyl

2. The character of the substituent group in benzoic acid derivatives has a larger effect on solubility and adsorption than does the position of one and the same substituent in the acid.

3. The functional group polarity and its possibility of forming hydrogen bonds has a large effect on the adsorption and solubility of benzoic acid derivatives.

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Received December 16, 1952.

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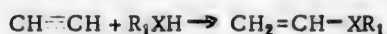
SYNTHESIS AND TRANSFORMATION OF α -METHYLVINYL BUTYL ETHER. II.

M. F. Shostakovsky and E. P. Gracheva

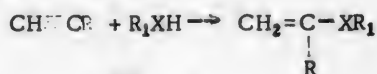
Among various unsaturated compounds having reactive properties, compounds whose structures contain one or two substituents on a vinyl group carbon are of great interest.

The simplest procedure for obtaining these compounds (I, II) is by reacting acetylene and monosubstituted acetylenic hydrocarbons with alcohols, acids, mercaptans, amines, and other compounds containing labile hydrogen [1, 2, 3, 4].

In all of these cases, reaction takes place according to the scheme:



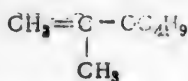
(I)



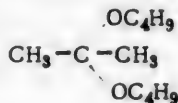
(II)

where R is an alkyl or aryl group, X is a hetero O, N, S, or other atom, and R_1 is the radical from the acid, alcohol, mercaptan, etc.

The goal of the present study is further development of the A. E. Favorsky and M. F. Shostakovsky [2] vinyl-ation reaction and extension of the synthesis of α -substituted vinyl ethers, particularly the synthesis of α -methyl vinyl butyl ether (III) and its derivative dimethyldibutoxyketal (IV).



(III)



(IV)

Compound (III), like other representatives of this homologous series [5] is of interest for studying reactivity with regard to addition and hydrolysis reactions.

Preparation of α -substituted vinyl compounds indicates that existence of reaction between methylacetylene and alcohol requires more severe conditions than were established by A. E. Favorsky and M. F. Shostakovsky for the corresponding reaction with acetylene.

This observation is in complete agreement with the proposal of M. F. Shostakovsky with regard to reactivity of chemical compounds, which depends on the number of reactive centers in the molecule (the number of functional groups with labile hydrogen).

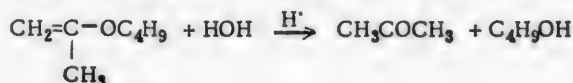
Based on reaction adding butyl alcohol to α -methylvinyl butyl ether under the influence of mineral acid (HCl), it was established that this reaction is exothermal and leads to forming dimethyldibutoxyketal (IV) in good yield. As regards procedures for obtaining this ketal, some data can be found in the literature on this question.

Claisen [6] described a general method for preparing acetals of aldehydes and ketones based on reacting the latter with orthoformic esters in an ether solution.

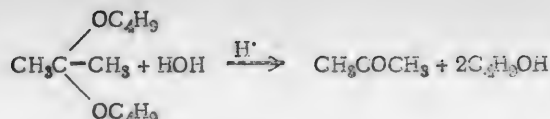
A. E. Arbuzov [7], working on obtaining the ketal of acetone (according to the Claisen procedure), improved the cited synthesis by showing that this reaction was catalytic and brought the addition of mineral acid (HCl, H_2SO_4) to its necessary catalytic minimum.

Nieuwland and coworkers [8] describe in a number of papers the preparation of ketals based on alkylacetylenes and alcohols in presence of mercury oxide and BF_3 .

The authors of the present paper made the observation that the α -methylvinyl butyl ether prepared* and its derivative - dimethyldibutoxyketal - readily hydrolyze in presence of water or dilute acids:



* Not previously reported in the literature.



In the literature, hydrolysis of α -substituted vinyl ethers is discussed in a number of studies by A. M. Butlerov [9], A. P. Eltekov [10], and A. E. Favorsky [11]. A. E. Arbuzov [7] studied in detail the dissociation of ketals under action of dilute sulfuric acids. Claisen [6] noted the ease of hydrolyzing the ketals he prepared.

EXPERIMENTAL

1. Initial substances and method of synthesis

Butyl alcohol (b.p. 117° , d_4^{20} 0.830, n_D^{20} 1.3988) and methylacetylene (b.p. -28°) were used as raw materials for synthesis of α -methylvinyl butyl ether and its ketal.

Methylacetylene was prepared by the method of Hurd and Spence [12], by brominating propylene and subsequently splitting out two molecules of hydrogen bromide. The methylacetylene obtained in this manner was dried by passage through a column filled with calcium chloride and condensed in a receiver cooled with dry ice in a Dewar flask.

α -Methylvinyl butyl ether was synthesized in an autoclave. Before charging with the corresponding quantity of alcohol (with catalyst), it was cooled in a freezing mixture (ice, salt) to -10 to -15° .

Working with methylacetylene was performed by cooling it with dry ice in an ampoule, previously weighed, which was introduced into the autoclave containing butyl alcohol and 10% powdered potassium hydroxide.

2. Synthesis of α -methylvinyl butyl ether (III)

Into a rotating Bergius-type autoclave, having 2.5 liter volume and fitted with electrical heating, thermocouples, and an acetylene pressure gauge, we charged 111 g (1.5 mole) butyl alcohol, 50 g (1.2 mole) methylacetylene, and 10 g powdered potassium hydroxide. The autoclave was heated for a 14 hour period at a temperature of $248-250^\circ$.

Time	Autoclave temperature, ($^\circ\text{C}$)	Autoclave pressure (atm)
0	0	7.0
0 hr 35 min	100	10.6
1 hr 10 min	135	15.2
2 hr 30 min	182	25.5
3 hr 30 min	225	38.0
4 hr 20 min	238	50.0
5 hr 05 min	348	58.0
	248	50.5
	250	43.0
	250	40.5

The dependence of pressure on temperature is given in the table.

It can be seen from the table that with increase in temperature a significant increase in autoclave pressure begins to occur. It reaches a maximum at 250° (58 atm). Thereafter, a gradual decrease in pressure was observed despite constancy of heating temperature.

After heating, the autoclave was cooled, and unreacted methylacetylene collected in a trap placed in a Dewar flask containing dry ice. 5.4 g methylacetylene was collected. The remaining reaction mass was transferred from the autoclave into a flask which was set in freezing mixture (snow + salt).

Distillation of the reaction mass was performed in a flask, with herringbone dephlegmator, in a Wood's metal bath.

The following fractions were collected: 1) b.p. $105-107^\circ$ (745.5 mm), 121.2 g; 2) b.p. $117-118^\circ$ (745.5 mm), 27.4 g; tarry residue, 11.8 g.

Investigation of fractions. The first fraction with a b.p. of $105-107^\circ$ (745.5 mm) was washed 8 times with water, dried with potash, and distilled in a column with an efficiency of 20 theoretical plates. In all, 90.7 g of the substance distilled at $111-112^\circ$ (751 mm).

n_D^{20} 1.4111; d_4^{20} 0.7955. Found: M 112.6 (cryoscopically). MR_D 35.80; %C 73.97; H 12.34. $C_7H_{14}O$. Calculated: M 114; MR_D 36.05; %C 73.70; H 12.40.

Hydrolysis of α -methylvinyl butyl ether. 20 g of the substance and 30 ml 1% H_2SO_4 solution were placed into a conical flask fitted with a ground stopper. The reaction mass was shaken for a period of 1 hour at room temperature, i.e., for the time necessary for the ether layer to disappear, after which the acid was neutralized

with calcined potash. The reaction product was salted out, extracted with ether, dried, and distilled in a flask with a herringbone dephlegmator on a water bath.

After distilling the solvent, a fraction was collected with b.p. 50-70°; this was dried over calcined potash and redistilled. After treating the separated substance with 2,4-dinitrophenylhydrazine, yellow-orange crystals precipitated; after three recrystallizations from alcohol, these had a 127.7° m.p., which corresponds to the 2,4-dinitrophenylhydrazone of acetone. Mixture tests gave no depression. The literature value [13] for the m.p. is 128°.

Thus, investigating the fraction having a 111-112° b.p. (751 mm) indicated that as a result of reacting methylacetylene with butyl alcohol in presence of KOH, synthesis of α -methylvinyl butyl ether occurs with a yield 75.8% of the theoretical.

3. Synthesis of Dimethyldibutoxyketal (IV).

Into a three-necked flask, fitted with mercury seal, reflux condenser, thermometer, and mechanical stirrer, we placed equimolecular quantities of α -methylvinyl butyl ether (11.4 g - 0.1 mole) and butyl alcohol (7.4 g - 0.1 mole). The mixture was thoroughly agitated for a 30-40 minute period and then catalyst (concentrated HCl) was added to the extent of two drops (0.04 g) at room temperature. After catalyst was added, the reaction mass temperature began to rise rapidly to 45-47° and then slowly fell to the initial room temperature.

In all, distillation separated 14.4 g of a substance having a 69-70° b.p. (24 mm); tarry residue was 2.7 g.

Investigation of the substance with b.p. 69-70° (24 mm). The product obtained was dried over calcined potash and distilled a second time at 70° (24 mm).

n_D^{20} 1.4150; d_4^{20} 0.8363. Found M 185.6 (cryoscopically); M_R 56.21. %C 70.12, 70.02; H 12.83, 13.05. $C_{12}H_{24}O_2$. Calculated: M 188; M_R 56.6; %C 70.2; H 12.8.

Hydrolysis of dimethyldibutoxyketal. A 25 g quantity of the substance and 60 ml of 1% H_2SO_4 solution were charged into an Erlenmeyer flask. The reaction mixture was shaken for a period of 1 hour, after which the acid was neutralized with a small amount of calcined potash, and the hydrolysis products distilled.

A broad fraction with 50-73° b.p. was collected in the amount of 2.77 g; this was dried with potash and treated with 2,4-dinitrophenylhydrazine; yellowish-red crystals precipitated, which after recrystallization from alcohol had m.p. 126.9°, which corresponds to the 2,4-dinitrophenylhydrazone of acetone.

Characteristics of the fraction boiling at 70° (24 mm) indicate that as a result of the interchange reaction between methylvinyl butyl ether and butyl alcohol in the presence of traces of HCl, synthesis of dimethyldibutoxyketal takes place with an 81% yield.

SUMMARY

1. Conditions were found for synthesis of α -methylvinyl butyl ether with a yield 75% of the theoretical.
2. Conditions were found for synthesis of dimethyldibutoxyketal with a yield 81% of the theoretical.
3. Hydrolysis of α -methylvinyl butyl ether or of dimethyldibutoxyketal leads to formation of the ketone and alcohol.

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Received April 25, 1953.

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• See Consultants Bureau English Translation, p. 1209.



ETHYLENEGLYCOLARSENOUS ACID ESTERS

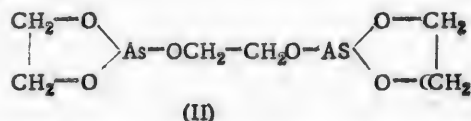
Gilm Kamal and Z. L. Khisamova

Detailed investigation of cyclic derivatives of arsenous acid was started in our laboratory in 1950 [1-2]. Cyclic esters of ethyleneglycolarsenous acid have not been studied by anyone. In the present paper, we present data obtained by us in studying acyl chlorides and mixed esters of ethyleneglycolarsenous acid, containing five-membered rings.

By action of an equimolar quantity of arsenic trichloride on ethylene glycol in an absolute ether medium in the presence of anhydrous pyridine, we synthesized the cyclic acid chloride of ethyleneglycolarsenous acid (I) as the main reaction product according to the equation:



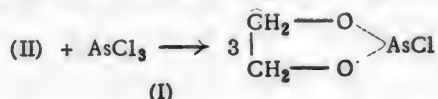
It was also found that in this reaction, in addition to the acid chloride, the complete ethylene glycol ester of arsenous acid was formed (II).



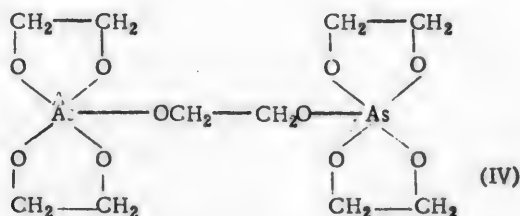
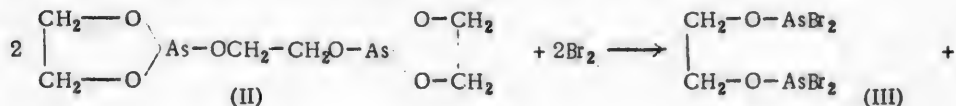
Experiments we performed on reacting the acid chloride of ethyleneglycolarsenous acid with ethylene glycol in presence of pyridine in an absolute ether medium led to the same final result. Thus, it was shown that ester (II) forms as a result of secondary reaction.

The complete ethylene glycol ester of arsenous acid (II) is also obtained in a very satisfactory yield of about 89-92% by direct reaction of arsenous anhydride on ethylene glycol at a temperature of 140-150°. This reaction is reversible; with excess water the ester completely hydrolyzes, forming arsenous anhydride.

Under the action of equimolar quantities of arsenic trichloride on (II), the acid chloride of ethyleneglycolarsenous acid (I) forms almost quantitatively according to the equation:



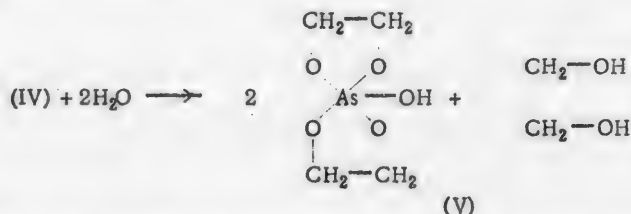
The ethylene glycol ester of arsenous acid (II) does not react on heating with methyl iodide and does not add sulfur or cuprous bromide. Its bromination reaction proceeds very unusually. Instead of the expected addition of two bromine molecules, exactly only half of the calculated quantity, i.e., one bromine molecule, adds in the given reaction. In this reaction, a very interesting transformation with complex radical rearrangement takes place. We previously [1] gave the following scheme for the course of reaction.



Formation of the acid bromide (III) under conditions of the experiment was actually shown. The acid bromide was a green-colored liquid with a mustard odor and b.p. 86° at 11 mm.

The second compound containing pentavalent arsenic separated by us formed glistening crystals with a 127° m.p. — readily soluble in many organic solvents and in water; it did not hydrolyze in the cold. Its aqueous solution had an acid reaction and could be titrated by 0.1 N NaOH solution. Doubts arose concerning the hypothetical structure previously given by us [1] for substance (IV). Further study showed that this compound was diethyleneglycolarsenous acid (V), described by Englund [3]. However, in contrast to Englund's preparation, our sample melted at 127°, and not 120°; its molecular weight, determined by the Rast method, was not double, but actually was close to the double value in a bromoform solution.

Formation of diethyleneglycolarsenous acid probably is via hydrolysis of the above-mentioned hypothetical compound (IV):



By reacting the acid chloride of ethyleneglycolarsenous acid (I) with the corresponding absolute alcohol in presence of pyridine in an ethyl ether medium, we synthesized various mixed esters of ethyleneglycolarsenous acid according to the following scheme:

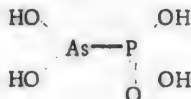


In this manner we separated methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-heptyl, n-octyl, nonyl, phenyl, and cyclohexyl esters of ethyleneglycolarsenous acid.

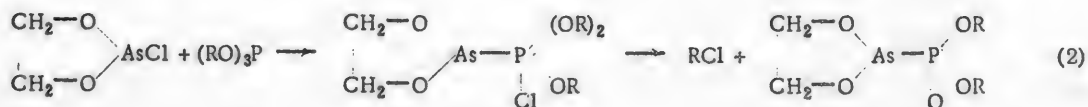
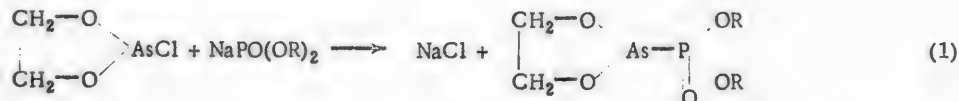
Under action of water, the above-cited esters decompose relatively readily, evolving heat and forming the corresponding alcohol, ethylene glycol, and arsenous anhydride:



We made attempts to perform reactions (1) and (2) for the purpose of preparing a derivative of the hypothetical imaginary acid:



but they remained unsuccessful.



EXPERIMENTAL

Preparation of the acid chloride of ethyleneglycolarsenous acid (I)

Into a round-bottom flask fitted with a reflux condenser, mechanical stirrer, and dropping funnel, we introduced 37.5 g of ethylene glycol, 87.2 g of anhydrous pyridine, and 400 ml of dry ether. 100 g arsenic trichloride was added dropwise with agitation and external cooling of the flask with ice and water. Cooling was discontinued

after the arsenic chloride was all introduced and the reaction mixture was heated on a water bath for a period of one hour and allowed to stand overnight. On the next day the ethereal solution was separated from the precipitate by decantation and the residue washed 3 times with absolute ether. The filtrate, after distilling the solvent, was subjected to vacuum distillation. As a result of distillation at 11 mm, the following fractions were separated: 1) 61.3 g with b.p. 70-76°; 2) 6.5 g with b.p. 76-160°; and 3) 10.3 g with b.p. 160-195°.

By doubly distilling the first fraction, we separated a substance with b.p. 71-72° at 11 mm, melting point 44-45°.

Found %: As 44.10; Cl 20.99. $C_2H_4O_2AsCl$. Calculated %: As 44.05; Cl 20.82.

The separated cyclic acid chloride of ethyleneglycolarsenous acid formed white, glistening, needle-shaped crystals readily soluble in ether, benzene, toluene, dichloroethane, and dioxane. The acid chloride immediately hydrolyzes in water, evolving heat and forming As_2O_3 (found %: As 75.21; calculated % As 75.73).

From the third, high-boiling fraction, we obtained a substance with a 166-167° b.p. at 4 mm (II), a colorless, viscous liquid:

d_4^{20} 1.8951; n_D^{20} 1.5433; MR_D 56.18; calculated 56.61. Found %: As 45.28. $C_6H_{12}O_6As_2$. Calculated %: As 45.40.

Preparation of the complete ethylene glycol ester of arsenous acid (III)

1) From the acid chloride of ethyleneglycolarsenous acid and ethylene glycol. The acid chloride of ethyleneglycolarsenous acid was added to a solution of 4.2 g of ethylene glycol and 10.4 g pyridine in 200 ml dry ether with mechanical agitation and cooling. After removing pyridine salts the filtrate was subjected to distillation. The main fraction had a b.p. of 166-167° at 4 mm.

2) From arsenous anhydride and ethylene glycol. 60 g arsenous anhydride and 86.4 g ethylene glycol were taken in a round-bottom Arbuzov flask. The flask was heated on an oil bath at 140-150° for a 30 minute period. A water aspirator was then connected for removing water formed in this reaction. After removing the water under vacuum and double distillation, we obtained 80.2 g of a fraction with b.p. 160-161° at 2 mm (92.4%).

Found %: As 45.47, 45.66. $C_6H_{12}O_6As_2$. Calculated %: As 45.40.

Action of arsenic trichloride on the complete ethylene glycol ester of arsenous acid. 15 g complete ethylene glycol ester of arsenous acid was placed in a round-bottom flask having a reflux condenser and dropping funnel. 6 g arsenic trichloride was added to it dropwise. At the end the contents of the flask were heated on a water bath for a 30 minute period. After cooling, the reaction mixture was vacuum distilled. The main fraction had b.p. 66-67° at 9 mm and m.p. 44-45°.

Found %: As 43.98; Cl 20.67. $C_2H_4O_2AsCl$. Calculated %: As 44.05; Cl 20.82.

Saponification of ester (II). 25 g arsenous acid ethylene glycol ester was boiled with 50 ml water for a period of 1 hour in a round-bottom flask with reflux condenser. The white precipitate separated was arsenous anhydride.

Found %: As 75.62. As_2O_3 . Calculated %: As 75.73.

Action of bromine on ester (II). 28 g bromine was added through a dropping funnel to 51 g ester dissolved in carbon tetrachloride. The reaction flask was cooled externally by snow. On adding each drop of bromine, an energetic reaction took place, with evolution of heat. Bromination was continued until appearance of a light yellow color. Needle-shaped crystals separated from the solution on standing. On the second day the crystals were filtered, pressed, and washed with carbon tetrachloride. The filtrate was subjected to vacuum distillation. 32.2 g was obtained in the main fraction having a b.p. of 86° at 11 mm. The substance separated was a slightly greenish colored liquid with a mustard odor, having lachrymatory properties.

d_0^0 2.6079; d_0^{20} 2.5668; n_D^{20} 1.6568.

Found %: As 28.38, 28.41; Br 60.39. $C_2H_4O_2As_2Br_4$. Calculated %: As 28.30; Br 60.36.

The needle-shaped crystals (V) obtained by us were then repeatedly recrystallized from hot toluene. Gleaming, white needles, with m.p. 127°, soluble in toluene, benzene, dioxane, acetone, chloroform, ethyl alcohol, and water; poorly soluble in ether. The water solution had an acid reaction (Congo red turns intense blue).

Found %: As 35.62, 35.63. $C_4H_8O_5As$. Calculated %: As 35.42.

0.2255 g substance: 10.75 ml 0.1 N NaOH. Found: equimolecular weight 210.82. Found M 210.41, 211.25 (Rast); 378.4, 375.6 (cryoscopically in bromoform). $C_4H_8O_5As$. Calculated: M 212.03.

By reacting 1.5 g brucine in a methyl alcohol solution with 0.807 g diethyleneglycolarsenous acid (V), we obtained a salt with m.p. about 204°, which corresponds to the data of England [3].

Found %: As 11.82, 11.63. $C_{28}H_{26}O_4N_2(C_2H_4O_2)_2AsOH \cdot CH_3OH$. Calculated %: As 11.75.

Preparation of ethyleneglycolarsenous acid methyl ester

20 g of the acid chloride of ethyleneglycolarsenous acid (I) dissolved in 50 ml ethyl ether was added through a dropping funnel to 3.8 g methyl alcohol, 9.2 g anhydrous pyridine, and 250 ml absolute ethyl ether cooled to 0°. After adding the entire quantity of acid chloride, the reaction mixture was heated on a water bath for a period of one hour. On the next day the pyridine hydrochloride was filtered off and washed 3 times with dry ether. After distilling the solvent, the remaining liquid was vacuum distilled. 8.6 g of a fraction was obtained with b.p. 50-51° at 11 mm. Ethyleneglycolarsenous acid methyl ester was a mobile liquid. It was readily hydrolyzed by water, forming arsenous anhydride.

Preparation of other esters of ethyleneglycolarsenous acid was conducted by the method described, starting with the corresponding alcohol, 9.2-9.3 g dry pyridine, and 20 g of the acid chloride of ethyleneglycolarsenous acid (I) in 200-300 ml ethyl ether.

The esters obtained were colorless liquids (beginning with the hexyl ester they had a thick consistency), and odorless (except for the nonyl ester, which had a pleasant odor).

Data for the esters prepared are given in the table.

Esters of Ethyleneglycolarsenous Acid

Ester	Formula	Alcohol taken for reaction (g)	Ester yield (g)	B.p., °C	Pressure (mm)	d_4^{20}	d_4^{20}	n_D^{20}	MR _D		As content (%)	
									Found	Calculated	Found	Calculated
Methyl	$C_3H_7O_3As$	3.8	8.6	50-51	11	1.6453	1.6310	1.4935	29.25	29.41	44.72	45.09
Ethyl *	$C_4H_9O_3As$	9.5	19	61-62	11	1.5031	1.4784	1.4788	34.50	34.03	41.54	41.61
											41.71	
n-Propyl	$C_5H_{11}O_3As$	7	—	74-75	12	1.4188	1.3923	1.4762	39.33	38.64	38.85	38.60
n-Butyl	$C_6H_{13}O_3As$	8.7	11	93	16	1.4024	1.3764	1.4785	42.82	43.26	36.31	36.00
n-Hexyl	$C_8H_{17}O_3As$	12	17	120-121	10	1.3033	1.2813	1.4742	51.86	52.49	31.63	31.72
n-Heptyl	$C_9H_{19}O_3As$	13.7	21.8	130-131	11	1.2671	1.2465	1.4736	56.37	57.14	29.80	29.94
n-Octyl**	$C_{10}H_{21}O_3As$	15.2	14	110	2	1.2449	1.2250	1.4737	61.44	61.73	28.41	28.34
n-Nonyl	$C_{11}H_{23}O_3As$	17	15.6	117-118	2	1.2240	1.2041	1.4748	—	—	27.33	27.03
Cyclo-hexyl***	$C_6H_{12}O_3As$	8.8	—	118	11	1.4270	1.4044	1.5070	—	—	31.84	32.00
Phenyl	$C_6H_5O_3As$	11	6.3	143-144	12	1.5687	1.5440	1.5716	—	—	32.70	32.85

* 16.4 g pyridine and 35 g acid chloride (I) were taken for the reaction.

** 6.7 g pyridine taken for reaction.

*** 6.9 g pyridine and 15 g acid chloride (I) were taken for reaction.

Experiment on reacting ethyleneglycolarsenous acid methyl ester with methyl iodide

5 g ethyleneglycolarsenous acid methyl ester and 8 g methyl iodide were heated in a flask with reflux condenser on a water bath for a period of 6 hours. On distillation, according to data on boiling points and refractive indices, the initial substances were recovered. It was not possible to separate any other individual substance.

Action of bromine on ethyleneglycolarsenous acid ethyl ester

5 g ethyleneglycolarsenous acid ethyl ester and 20 ml of carbon tetrachloride were placed in a round-bottom flask of 50 ml capacity. 4.4 g bromine was added through a dropping funnel. Vigorous heating was observed. The carbon tetrachloride was distilled at normal pressure. The remaining liquid was distilled under vacuum. The main fraction boiled at 72-73° at 14 mm.

The addition product was a heavy, light-yellow colored liquid.

d_4^{20} 2.2152; d_4^{20} 2.1767; n_D^{20} 1.5880.

Found %: As 22.09; Br 46.69. $C_4H_2O_3AsBr_2$. Calculated %: As 22.04; Br 47.03.

Action of the acid chloride of ethyleneglycolarsenous acid
on the butyl ester of phosphorous acid

15 g tributylphosphite dissolved in 200 ml ethyl ether was taken in a round-bottom flask fitted with reflux condenser and dropping funnel. After cooling to -13° (ice + salt), 10.3 g acid chloride of ethyleneglycolarsenous acid was then added, half diluted with ether. The exchange reaction takes place very vigorously. The reaction mass at first is noticeably yellow, and then becomes brown. A precipitate of red phosphorus separated on standing. The precipitate was filtered. The filtrate was subjected to distillation. After removing the ether at normal pressure, a fraction was obtained boiling at $117-121^\circ$ (d_4^{20} 0.8099, n_D^{20} 1.4015), which corresponded to butyl alcohol. Subsequently, the following fraction was separated by vacuum distillation: b.p. 140° at 5 mm; d_4^{20} 1.1185, n_D^{20} 1.4333. The substance contains arsenic and phosphorus, but it readily decomposes forming a black residue.

Reacting the acid chloride of ethyleneglycolarsenous acid
with the Na-derivative of diethylphosphorous acid

200 ml dry ethyl ether and 4.1 g metallic sodium were placed in a reaction flask. 24.5 g diethylphosphorous acid was then added from a dropping funnel.

A 30 g quantity of the acid chloride of ethyleneglycolarsenous acid, half diluted with ether, was added dropwise with external cooling to the Na-derivative of diethylphosphorous acid. The contents of the flask first turned yellow during the addition, and at the end acquired a brick-red color. The residue -sodium chloride - was filtered off. After drying, its pure weight was 9.9 g (theoretically required 10.3 g). Strong decomposition took place during distillation under vacuum. It was not possible to separate individual substances.

SUMMARY

1. It was shown that by reacting ethylene glycol with arsenic trichloride in an absolute ether medium and in the presence of pyridine, it was possible to obtain the acid chloride of ethyleneglycolarsenous acid and the complete ethylene glycol ester of arsenous acid.

2. A simpler and more convenient method for preparing the ethylene glycol ester of arsenous acid was developed by means of reacting ethylene glycol with arsenous anhydride.

3. The bromination reaction of the arsenous acid ethylene glycol ester was studied. In this reaction an acid bromide having the composition $[-CH_2OAsBr_2]_2$ was separated, and also diethyleneglycolarsenous acid.

4. Cyclic mixed esters were synthesized having the composition

$$\begin{array}{c} CH_2-C \\ | \\ CH_2-O \end{array} AsOR, \text{ and their reactions}$$

and properties described.

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Received January 6, 1953

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TERTIARY TRIHYDRIC ALCOHOLS OF THE ACETYLENIC SERIES AND THEIR TRANSFORMATIONS

III. POTASSIUM PERMANGANATE OXIDATION

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It was shown in our earlier papers [1,2] that the A.E.Favorsky reaction — the reaction of acetylene with ketones in a dry ether medium in presence of powdered potassium hydroxide — could be varied to prepare tertiary trihydric alcohols of the acetylenic series, if a ketoalcohol were used instead of the ketone, and an acetylenic alcohol used in place of acetylene.

In systematically studying chemical transformations of acetylenic glycerols, we encountered the need to have a clear picture of the manner in which their oxidation by potassium permanganate occurred.

In the last ten or fifteen years, enough papers have already appeared in the chemical literature dealing with the question of oxidation of triple bonds in acetylenic hydrocarbons, alcohols, and particularly, in glycols. Without doubt, these introduced some clarity into the question being discussed here by us. However, these investigations, in the first place, frequently did not have a systematic character, and, in the second place, of the hydroxyl-containing acetylene derivatives, they refer almost exclusively to γ -glycols; they hardly touch at all upon questions of oxidizing acetylenic α -glycols, erythritols, and trihydric alcohols.

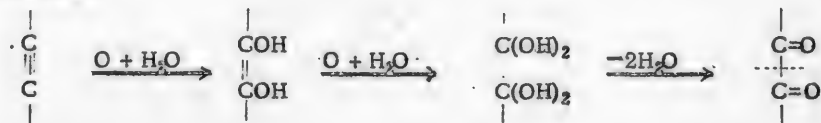
Attempts to formulate a scheme for oxidation of triple bonds by potassium permanganate were already undertaken by E. E. Vagner, who, in his classical investigations on oxidizing olefins, tried also to give a probable scheme of oxidation for hydrocarbons of the acetylene and allene classes. However, one can hardly agree entirely with his scheme.

Vagner proposed that in the first phase of acetylene oxidation, addition of the elements of hydrogen peroxide to it would occur, with formation of an unsaturated glycol incapable of independent existence, which on hydration would be transformed into a hydrated form of a glycollic aldehyde; the latter would then lose water, and, depending on the order in which this water evolution occurred, either oxalic or acetic acid would be formed.

V. N. Krestinsky and M. K. Kelbovskaya [3] undertook attempts to separate any neutral products from the oxidation of acetylenic hydrocarbons. They oxidized acetylene, phenylacetylene, methylethylacetylene, and tertiary butylacetylene. However, they were not able to separate any neutral products on the basis of which it would be possible to formulate conclusions on the specific mechanism of this process. They only separated acids.

The authors proposed that the primary products of adding the elements of the oxidant to the triple bond evidently undergo hydrolysis, forming acids corresponding to breakdown at the triple bond location.

It seems to us that it is simpler to assume for acetylenic bond oxidation, following Vagner, the formation of neutral glycols in a first phase which, naturally, in view of the energetic oxidizing medium, are not able to undergo all the transformations Vagner describes; having a double bond, they are more readily split because of the presence of two hydroxyl groups, and are immediately subjected to further oxidative action by the potassium permanganate. Addition of two more water residues to the double bond occurs, with subsequent separation of water and formation of a diketone, which then oxidizes further to the acid usually obtained on oxidation of acetylene or acetylenic hydrocarbons.



In case there are hydroxyl groups adjacent to the triple bond present in the molecule, then the oxidation

process is somewhat complicated by secondary reactions as a result of which neutral substances may appear among the oxidation products, in addition to acids.

DuPont [4] and V. N. Krestinsky and N. Persiantseva [5], on oxidizing tetramethylbutynediol with potassium permanganate, obtained acetone and oxalic acid, in addition to α -hydroxyisobutyric acid. This circumstance forced them to assume the presence of two tautomeric forms in tetramethylbutynediol.

However, none of the facts given in the literature confirms the accuracy of this assumption, with the exception of the fact that oxalic acid and acetone are obtained on oxidation. However, their formation can be completely explained without assuming tautomeric forms. On the other hand, experimental material has been accumulating during recent years which, like the data obtained by us and published below, directly shows the absence of these tautomeric forms, both from tertiary acetylenic γ -glycols and from other structurally similar acetylene hydroxyl derivatives.

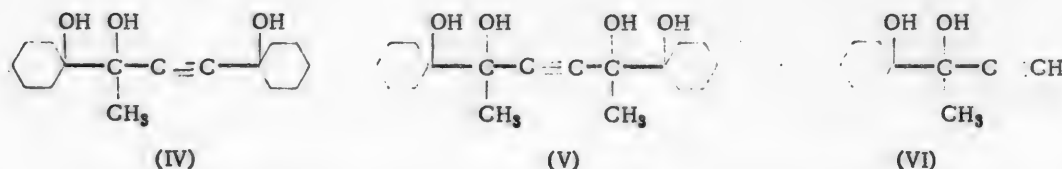
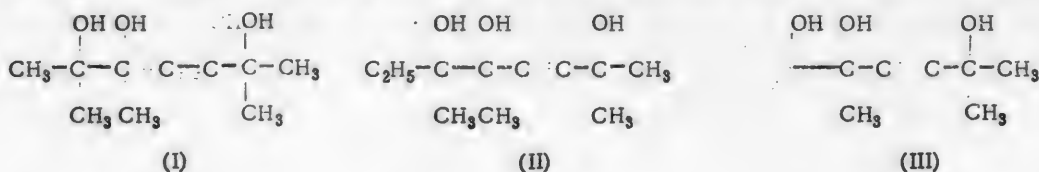
T. I. Temnikova and P. A. Tikhomolov [6] performed the oxidation of tetratolylbutynediol with chromic anhydride in acetic acid; they were able to separate a cyclic α -diketone.

P. A. Tikhomolov and A. E. Druzhinin [7] under the same conditions, likewise obtained a corresponding α -diketone by oxidizing tetraphenylbutynediol.

Yu. S. Zalkind and P. S. Bataev [8] separated free diketone after oxidizing tetraphenylbutynediol ethers with chromic anhydride.

S. A. Zonis [9] studied the oxidizing action of manganese triacetate on acetylenic γ -glycols. He showed that in oxidizing ditertiary acetylenic γ -glycols of the aromatic or aliphatic-aromatic series, manganese triacetate acts as an acetylating agent on the triple bond; a diacetyl derivative of a substituted dihydrofuran is formed. In case manganese triacetate acts on ditertiary γ -glycols of the aliphatic series, oxidation proceeds otherwise, and leads to destruction of the carbon chain. On oxidizing a disubstituted acetylenic γ -glycol with the same oxidant, Zonis obtained acetylenic diketones.

In the present study, we oxidized 6 tertiary alcohols of the acetylenic series with potassium permanganate:



2,3,6-Trimethylheptyne-4-triol-2,3,6 (I). Acetone and dimethylacetylcarbinol were obtained, and acetic, formic, oxalic, and α -hydroxyisobutyric acids.

3,4,7-Trimethyloctyne-5-triol-3,4,7 (II). We obtained acetone, methyl ethyl ketone, and methylethylacetylcarbinol, as well as acetic, formic, oxalic, and α -hydroxyisobutyric acids.

2,5-Dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol-2,5 (III). We obtained acetylcyclohexanol, cyclohexanone, and acetone, as well as formic, acetic, oxalic, and α -hydroxyisobutyric acids.

2,4-Di-(1-hydroxycyclohexyl)-butyne-3-ol-2 (IV). We obtained acetylcyclohexanol, cyclohexanone, and acetic, oxalic, α -hydroxyhexahydrobenzoic, and adipic acids.

2,5-Di-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (V) (in acetone solution). We obtained acetylcyclohexanol, and cyclohexanone, and formic, acetic, oxalic, and adipic acids.

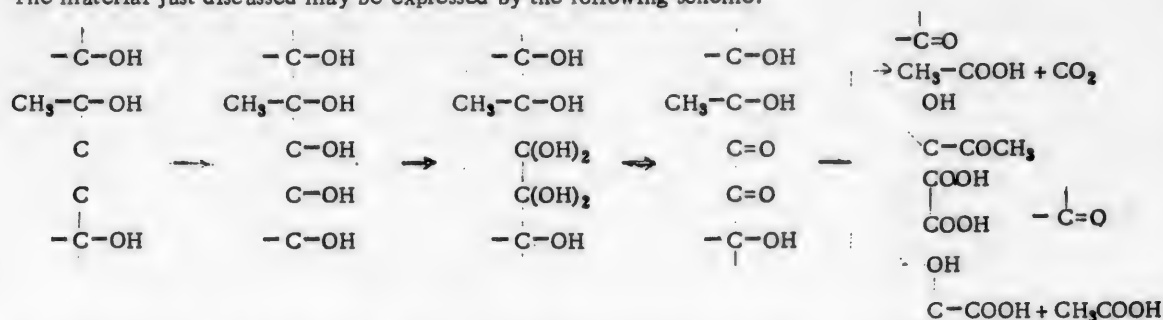
2-(1-Hydroxycyclohexyl)-butyne-3-ol-2 (VI). We obtained acetylcyclohexanol and cyclohexanone; formic, acetic, oxalic, and adipic acids.

Thus, oxalic acid was obtained in all six cases of oxidation. Its formation in the sixth, last, case could be explained by the presence of tautomeric forms as proposed by DuPont, Krestinsky, and Persiantseva. It has been

shown in our laboratory that tertiary trihydric alcohols of the ethylenic series, where the possibility of the cited tautomerization is completely excluded, also give oxalic acid on oxidation by potassium permanganate.

Consequently, the matter is not one of tautomerization. Starting with the data obtained by us, and also based on the fact that a number of authors, in oxidizing some acetylenic γ -glycols, were able to separate saturated diketones, it is necessary to assume that the acetylenic bond oxidizes in the very same manner in hydroxyl-containing acetylene derivatives as it does in acetylenic hydrocarbons. This scheme in the case of permanganate oxidation does not differ in principle from the scheme of oxidizing double bonds in ethylenic hydrocarbons, as developed by Vagner, i.e., in the first reaction phase the elements of hydrogen peroxide add to the triple bond. The unsaturated glycol formed, which is then subjected to further oxidative action, again adds the elements of hydrogen peroxide to the double bond, and thus transforms into a diketone. Subsequent oxidative attack, evidently, is directed at carbon bonds both between carbon atoms having carbonyl oxygen atoms, and between carbon atoms on one of which there is a carbonyl oxygen, and on the other a hydroxyl group. Oxidation takes place likewise even at bonds between carbon atoms both of which have hydroxyl oxygen.

The material just discussed may be expressed by the following scheme:



At the same time, judging from the quantity of α -hydroxyisobutyric acid (or α -hydroxyhexahydrobenzoic acid, respectively) which is separated as a result of oxidation to the extent of more than half a mole per mole of substance oxidized (see table), it should be concluded that the oxidant action is mainly directed at the bond between carbons carrying ketonic oxygens.

Alcohol oxidized	Quantity of substance (g)	Obtained		NaOH (g) used in titrating the volatile acids, calculated per mole of substance oxidized
		α -hydroxyisobutyric acid (g), calculated per mole of substance oxidized	Oxalic acid (g), calculated per mole of substance oxidized	
I	16.49	52.7	6.7	8.57
II	13.9	59.0	13.6	11.1
III	16.9	56.1	42.8	7.38
IV	17.4	67.6*	23.5	2.15
V	6.0	—	46.5	2.96
VI	4.7	—	14.3	8.0

* The acid was α -hydroxyhexahydrobenzoic.

Moreover, it follows from the table presented that oxalic acid is formed comparatively slightly in the case when the acetylenic alcohol being oxidized contains an aliphatic radical, and that formic and acetic acids are formed to a significantly greater extent. The same results are obtained in the case where a mono-substituted hydroxyl derivative of acetylene is oxidized. Introducing a cyclic alcohol group as the substituting radical somewhat increases oxalic acid formation. Here the quantity of volatile acid is significantly decreased; this can be seen from the quantity of sodium hydroxide used for titrating the volatile acids, the quantity of which has been calculated per mole of substance oxidized.

As regards formic acid, its formation should be attributed somewhat to the partial oxidation of acetone, which is either obtained as a result of reaction or is introduced into the reaction as a solvent. The ability of acetone to be oxidized by potassium permanganate was shown by Evans and Nicoll [10], who found that in acid or neutral media acetone was oxidized by permanganate to acetic acid and CO_2 . Formation of the latter in this case must be considered as a result of further oxidation of formic acid.

From (VI), formic acid is formed because of direct oxidation of the α -glycol at the triple bond.

Adipic acid is formed from (IV) and (V) as the result of subsequent partial oxidation of cyclohexanone.

EXPERIMENTAL

Oxidation of 2,3,6-trimethylheptyne-4-triol-2,3,6 (I).

20 g of 2,3,6-trimethylheptyne-4-triol-2,3,6, with m.p. of 82-83°, dissolved in 100 ml of water, was introduced into a liter flask fitted with mechanical stirrer, and then 1134 ml of 3% potassium permanganate solution was added slowly dropwise (based on calculating 3 active oxygen atoms per alcohol molecule). Oxidation took place at room temperature. After addition of all the potassium permanganate solution, the transparent solution was filtered from the precipitated manganese dioxide deposit; the precipitate was washed several times with hot water.

A distillate of neutral products was distilled from the filtrate and the acid salts extracted by ether in an extractor to complete the extraction of all neutral products possibly remaining.

After drying and distilling the ether, 3.51 g crystals remained, with m.p. 82-83°; they were shown to be the initial alcohol. Thus, 16.49 g of the triol entered the oxidation reaction.

The distillate containing the neutral products was salted out with sodium sulfate and repeatedly distilled, each time to half its volume, until the volume of the distillate reached 200 ml. After this the low-boiling products were distilled from the distillate in a rectification column with an effectiveness of 22 theoretical plates.

The following fractions were collected: 1) 0.55 g, b.p. 53-54°; 2) 2.8 g, b.p. 54-78°.

From the first fraction a semicarbazone was obtained with a m.p. of 185-187°. A mixed test with the semicarbazone of known acetone melted at 185-187°. In addition, a 2,4-dinitrophenylhydrazone was obtained with m.p. 124-126°; a mixed test with the 2,4-dinitrophenylhydrazone of known acetone did not give a melting point depression.

The aqueous fraction remaining after distilling the readily volatile neutral products was saturated with sodium sulfate and extracted with ether in an extractor until neutral products were completely extracted. The ether extracts were dried and the residual liquid, after distilling the ether, (1.2 g) distilled at normal pressure. The following fractions were obtained:

1) B.p. to 135°; n_D^{20} 1.4130; 2) b.p. 135-139°; n_D^{20} 1.4162.

From the second fraction we obtained a semicarbazone in the form of transparent crystals which after recrystallization from methyl alcohol melted at 160-161° and did not give a depression on melting with the semicarbazone of known dimethylacetylcarbinol.

The acid salts were acidified with hydrochloric acid and the volatile acids steam distilled. The steam-distilled distillate containing volatile acids was neutralized with 180.95 ml standardized sodium hydroxide solution (0.1052 N); this corresponds to 0.7602 g sodium hydroxide. The presence of formic acid was shown by obtaining a calomel precipitate, and the presence of acetic acid — by the cacodyl oxide reaction.

The non-volatile acids were neutralized with sodium hydroxide, heated to 70-80°, and, using a saturated calcium chloride solution, oxalic acid was precipitated as its calcium salt, from which 0.6 g oxalic acid was obtained with a m.p. of 101-102°. Mixture tests with known oxalic acid did not show depression. The filtrate after separating the calcium oxalate salt was acidified with hydrochloric acid and extracted with ether in an extractor. The separated crystals (4.7 g) after recrystallization from benzene melted at 79° and did not give a depression on fusion with known α -hydroxyisobutyric acid.

Thus, as a result of oxidizing 2,3,6-trimethylheptyne-4-triol-2,3,6, acetone and dimethylacetylcarbinol were obtained from the neutral products, and acetic, formic, oxalic, and α -hydroxyisobutyric acids from the acid products.

Oxidation of 3,4,7-trimethyl-octyne-5-triol-3,4,7 (II).

1053 ml of 3% potassium permanganate solution was slowly added dropwise to 20 g of freshly distilled triol with a b.p. of 135-136° at 3-4 mm, dissolved in 100 ml water (based on calculating three active oxygen atoms per octynetriol molecule).

Separation and investigation of oxidation products was performed in the same manner as in the previous

experiment; 6.1 g triol was recovered, consequently 13.9 g of the substance entered the reaction.

The following fractions were taken from the column on distilling the distillate containing neutral products: 1) 0.8 g with b.p. 53-56°; 2) 0.5 g with b.p. 56-71°; 3) 0.8 g with b.p. 71-81°.

A semicarbazone and a 2,4-dinitrophenylhydrazone were obtained from the first fraction; these melted at 185-187° and 124-125°, respectively, and corresponded to acetone.

A 2,4-dinitrophenylhydrazone with m.p. 112-113° was obtained from the second and third fraction; this corresponds to the 2,4-dinitrophenylhydrazone of methyl ethyl ketone (mixture tests).

5.2 g of a substance was separated from the solution after distilling the readily volatile products in the column; on distillation of this, the following fractions were collected: 1) 0.4 g with b.p. up to 60°; 2) 0.2 g with b.p. from 60 to 80°, n_D^{20} 1.3848; 3) 1.2 g with b.p. 80-146°; 4) 1.6 g with b.p. 146-149°, n_D^{20} 1.4210; residue 0.6 g.

The second fraction corresponds to methyl ethyl ketone according to its refractive index (literature data: n_D^{20} 1.3839). The 2,4-dinitrophenylhydrazone of methyl ethyl ketone was obtained from this fraction and melted at 112-113°.

According to its refractive index, the fourth fraction corresponds to methylethylacetylcarbinol (literature data: n_D^{20} 1.4220). The 2,4-dinitrophenylhydrazone melts at 107-108° and corresponds to the 2,4-dinitrophenylhydrazone of methylethylacetylcarbinol (mixture test).

The distillate containing volatile acids was neutralized with 185.92 ml standardized sodium hydroxide solution (0.0970 N); this corresponds to 0.7214 g sodium hydroxide. Presence of formic and acetic acids was shown qualitatively, by preparation of calomel and cacodyl oxide.

0.95 g oxalic acid with m.p. of 101-102° (mixture test) and 4.1 g α -hydroxyisobutyric acid melting at 79° (mixture test) were separated from the non-volatile acids).

Thus, as a result of oxidizing 3,4,7-trimethyloctyne-5-triol-3,4,7, acetone, methyl ethyl ketone, and methylethylacetylcarbinol were obtained among the neutral products and acetic, formic, oxalic, and α -hydroxyisobutyric acids among the acid products.

Oxidation of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol-2,5 (III).

20 g of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol-2,5 (m.p. 87-88°) was dissolved in 100 ml water, and then 934 ml 3% potassium permanganate solution was gradually added dropwise (based on calculating three active oxygen atoms per alcohol molecule).

Separation and investigation of oxidation products was similar to the previous experiments. 3.1 g of unreacted starting substance was recovered (m.p. 87-88°).

A fraction weighing 0.7 g with b.p. 52-53° was distilled in a column from the distillate containing neutral products; its semicarbazone was obtained by the Zelinsky method. The crystals, recrystallized from methyl alcohol, melted at 185-187°; mixture tests with the semicarbazone of known acetone did not show melting point depression.

The acetone obtained was also confirmed by preparing its 2,4-dinitrophenylhydrazone, which had a m.p. of 124-125° (mixture test).

From the solution remaining after distilling the acetone, 8.4 g of a substance was then extracted with ether. As a result of distillation (at normal pressure) these fractions were obtained: 1) 1.2 g with b.p. 32-150°; 2) 1.4 g with b.p. 150-190°; 3) 4.85 g with b.p. 190-204°.

A semicarbazone having a m.p. of 160-163° was obtained from the second fraction; after recrystallization from methyl alcohol it melted at 165-166°, and did not show a depression in melting point when fused in a mixture with the semicarbazone of known cyclohexanone.

A semicarbazone was likewise obtained from the third fraction; recrystallized from methyl alcohol, it melted at 194-195° and did not give a depression on fusion with the semicarbazone of known acetylcyclohexanol.

A distillate containing volatile acids was distilled from the acid salts after acidification with hydrochloric acid; in neutralizing this 142.2 ml standardized sodium hydroxide solution (0.0970 N) was used, which corresponds to 0.5517 g sodium hydroxide. Presence of formic and acetic acids was shown by qualitative reactions — formation of precipitated calomel and cacodyl oxide.

3.2 g oxalic acid with a m.p. of 101-102° and 4.2 g α -hydroxyisobutyric acid with a m.p. of 79° (mixture test) were extracted from the non-volatile acids.

Thus, in oxidizing 2,5-dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol-2,5, acetone, cyclohexanone, acetylcyclohexanol, acetic acid, formic acid, oxalic acid, and α -hydroxyisobutyric acid were obtained.

Oxidation of 2,4-di-(1-hydroxycyclohexyl)-butyne-3-ol-2 (IV)

20 g of the substance and 100 ml water were placed in a liter flask and 790 ml 3% potassium permanganate solution added dropwise (based on calculating three active oxygen atoms per alcohol molecule). 2.6 g unreacted 2,3-di-(1-hydroxycyclohexyl)-butyne-3-ol-2 was recovered (m.p. 107-108°).

6.5 g of substance was separated from the distillate containing neutral products; in distillation of this, we obtained the fractions: 1) 0.25 g with b.p. 40-150°; 2) 1.5 g with b.p. 150-170°; n_D^{20} 1.4507; 3) b.p. 170-196°, 3.0 g.

The second fraction corresponds to cyclohexanone (literature data: n_D^{20} 1.4520). A semicarbazone was obtained from it — white crystals with m.p. 166-167° (mixture test).

From the third fraction (b.p. 170-196°) after a second distillation, we separated a fraction with b.p. 188-192° and n_D^{20} 1.4683, containing acetylcyclohexanol. (For known acetylcyclohexanol, n_D^{20} 1.4700). A semicarbazone was obtained in the form of transparent needle-shaped crystals melting at 194-195° (from methyl alcohol).

The distillate with volatile acids was neutralized with 44.16 ml standardized sodium hydroxide solution (0.1052 N); this corresponds to 0.1855 g sodium hydroxide. Presence of acetic acid was shown by obtaining cacodyl oxide. Formic acid was not detected.

After distilling volatile acids in a distillation flask, an oily layer floated on the surface which did not steam-distill, and which crystallized on cooling. The crystals (4.6 g), when recrystallized from benzene, melted at 105-106°. According to its melting point this acid corresponds to α -hydroxyhexahydrobenzoic acid [11].

The molecular weight of the acid with m.p. 105-106° was determined by titration.

0.0707 g substance: 7.7 ml 0.0675 N Ba(OH)₂. Found: M 139.5. C₇H₁₂O₃. Calculated M 144.

The barium salt was obtained; it contained 32.09% Ba. (C₇H₁₁O₃)₂Ba. Calculated %: Ba 32.45.

After separating the α -hydroxyhexahydrobenzoic acid from solution, oxalic acid was separated (1.6 g, with m.p. 101-102°), and 2.9 g of crystals which after recrystallization from ethyl acetate, melted at 150-152° and were shown to be adipic acid (mixture test).

Thus, as the result of oxidizing 2,4-di-(1-hydroxycyclohexyl)-butyne-3-ol-2, cyclohexanone and acetylcyclohexanol were obtained, together with the acids: α -hydroxyhexahydrobenzoic, oxalic, adipic, and a small amount of acetic.

Oxidation of 2,5-di-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (V)

In view of the fact that this erythritol is not soluble in water, we performed its oxidation in acetone. 8.5 g of the erythritol having a m.p. of 161-162° and 300 ml acetone previously distilled over potassium permanganate were introduced into the flask. Then potassium permanganate (8.7 g) was introduced with continuous agitation and in small portions over a 6 hour period (based on calculating three active oxygen atoms per molecule of the erythritol). Oxidation took place at room temperature. The translucent acetone solution was filtered from precipitated manganese dioxide; the latter was washed with acetone and then several times with hot water. After distilling the acetone, a liquid (6.3 g) remained in the flask from which crystals separated (1.7 g); these were shown to be the starting unoxidized erythritol (mixture test). The liquid, after separating unreacted erythritol, was distilled at normal pressure. We collected the fractions: 1) 0.6 g with b.p. 130-150°; 2) 0.95 g with b.p. 150-155°, n_D^{20} 1.4510; 3) 0.7 g with b.p. 155-195°; 4) 1.3 g with b.p. 195-200°, n_D^{20} 1.4692; residue 0.8 g.

The second fraction is cyclohexanone; its semicarbazone was obtained by the Zelinsky method. The crystals after recrystallization melted at 165-166°, and did not give a depression when fused with the semicarbazone obtained from known cyclohexanone.

The fourth fraction was shown to be acetylcyclohexanol; a semicarbazone was obtained from it with m.p. 194-195° (mixture test).

The water solution which contained the acid salts was extracted with ether in an extractor for extraction of possibly unoxidized erythritol. After this the supplemental ether was distilled, and 0.8 g crystals with m.p. 161-162° was separated, corresponding to the initial erythritol. Consequently, 2.5 g of unoxidized substance was

recovered from the 8.5 g taken for the reaction. The water solution was acidified with hydrochloric acid, and the volatile acids steam distilled. The distillate was neutralized with a sodium hydroxide solution. 121.8 ml sodium hydroxide (0.1176 N) was used in neutralization — corresponding to 0.5737 g sodium hydroxide.

Presence of acetic and formic acids was shown qualitatively, although the calomel precipitate was rather small.

0.9 g oxalic acid with a m.p. of 101-102° and 0.3 g adipic acid with m.p. 151-152° were separated from the non-volatile acids.

Thus, by oxidizing 2,5-di-(1-hydroxycyclohexyl) hexyne-3-diol-2,5, cyclohexanone, acetylcyclohexanol, oxalic acid, acetic acid, traces of formic acid, and adipic acid were obtained (the last as the product of oxidation of cyclohexanone).

Oxidation of 2-(1-hydroxycyclohexyl)-butyne-3-ol-2 (VI)

6 g of the glycol (m.p. 67-68°) dissolved in 50 ml water was placed in a flask and 377 ml 3% potassium permanganate solution (three active oxygen atoms per glycol molecule) gradually added. Separation and investigation of reaction products were similar to the foregoing. 1.3 g of a thick liquid which crystallized on standing was recovered from the reaction; the crystals melted at 67° and were unreacted α -glycol.

2.8 g of a substance was separated from the distillate which contained the neutral products; on its distillation, the following fractions were collected.

1) 0.3 g, b.p. 40-150°; 2) 0.3 g, b.p. 150-175°; 3) 0.5 g, b.p. 175-190°; 4) 1.1 g, b.p. 190-204°; residue 0.4 g.

The second fraction was cyclohexanone. A semicarbazone was prepared from it having a m.p. of 165-166° (mixture test).

The fourth fraction appeared to be acetylcyclohexanol; its semicarbazone melted at 194-195° (mixture test).

The distillate with volatile acids was titrated using sodium hydroxide solution (0.1176 N). 47.7 ml was used in neutralization — corresponding to 0.2247 g sodium hydroxide. Presence of formic and acetic acids were shown by qualitative reactions. Formic acid gave a voluminous calomel precipitate.

Oxalic acid (0.4 g) with m.p. 101-102° was separated from the nonvolatile acids, and mixture tests with commercial known oxalic acid did not show a depression. Moreover, 1.2 g of a liquid with a sharp acid odor was separated; it partly crystallized after lengthy standing. The separated crystals melted at 128-132°. In view of the small quantity, we were not able to purify it. In all probability, it was adipic acid.

Thus, on oxidizing 2-(1-hydroxycyclohexyl)-butyne-3-ol-2, cyclohexanone and acetylcyclohexanol were separated from the neutral products, and oxalic, acetic, and formic acids were separated from the acids.

SUMMARY

1. It is not necessary to consider that tautomeric forms actually exist, either for tertiary acetylenic γ -glycols as assumed by DuPont, Krestinsky, and Persiantseva, or for other tertiary polyhydric alcohols of the acetylenic series.

2. Tertiary acetylenic alcohols, α - and γ -glycols, glycerols, and erythritols are oxidized by potassium permanganate, evidently first of all to diketones, at the triple bond.

3. Oxidation does not halt at the stage of forming diketones and goes farther, on the one hand at bonds between carbons one of which has carbonyl oxygen and the other a hydroxyl; this causes formation of oxalic acid. On the other hand, it takes place on the bond between carbons having hydroxyl groups. The oxidation reaction mainly takes place on the bond between carbons with carbonyl oxygen, i.e., at the location of the triple bond in hydroxyl-containing acetylene derivatives.

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Received November 24, 1952.

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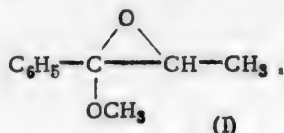
* See Consultants Bureau English Translation, p. 1311.

INVESTIGATIONS IN THE FIELD OF CYCLIC ACETALS OF HYDROXYCARBONYL COMPOUNDS

IV. DIMETHYLBENZOYLCARBINOL METHYL LACTOLIDE/AND ITS TRANSFORMATIONS

T. Temnikova and N. Almashi

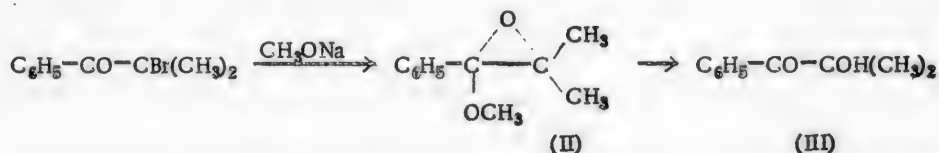
Methyl lactolides of α -ketoalcohols (α -methoxy or α -hydroxy) have hardly been studied. The methyl lactolide of methylbenzoylcarbinol (I)



the first example of this class of compounds whose structure has been rigidly established, was obtained comparatively recently by T. I. Temnikova and E. N. Kropacheva [1]. Study of the properties of this interesting compound is naturally difficult in view of its great tendency to polymerize. It was of interest to extend our investigation on chemical transformations of methyl lactolides of α -ketoalcohols, using a more stable substance as a basis; it could be expected, theoretically, that methyl lactolides of methylbenzoylcarbinol homologs which contained other hydrocarbon groups in place of the methyl would show less tendency to polymerize.

In the present research, we performed an investigation of the properties of dimethylbenzoylcarbinol methyl lactolide (II) and of its changes on reaction with various reagents.

The methyl lactolide of dimethylbenzoylcarbinol was prepared by the action of dry sodium methylate on α -bromoisopropyl phenyl ketone in absolute ether:



Dimethylbenzoylcarbinol methyl lactolide (1-methoxy-1-phenyl-2,2-dimethylethylene oxide) was a rather mobile liquid which did not change on extended storage.

Hydrolysis of the cyclic oxide occurs on heating the methyl lactolide (II) with 5% aqueous H_2SO_4 solution, and dimethylbenzoylcarbinol (III) is obtained.

To confirm the correctness of conclusions on structure for the substance obtained by reacting CH_3ONa with α -bromoisopropyl phenyl ketone, we performed spectrochemical investigations on it in the ultra-violet, based on our chemical data, and compared its absorption spectrum (Fig. 1, curve I) with the spectrum of dimethylbenzoylcarbinol (Fig. 1, curve II). The absorption spectrum of the substance obtained by reaction of CH_3ONa with α -bromoisopropyl phenyl ketone does not have an absorption maximum in the $\lambda = 270-290 \text{ m}\mu$ region; this indicates the absence of a carbonyl group in it. The substance absorbs only in the shorter wave region, on account of the benzene ring present in it. The absorption spectrum of dimethylbenzoylcarbinol is characterized by two maxima: at a $\lambda = 287 \text{ m}\mu$ and $320 \text{ m}\mu$, because of the presence of a benzoyl group in this substance.

Thus, spectrochemical study confirms as correct the conclusion that the substance obtained from reacting sodium methylate with α -bromoisopropyl phenyl ketone had a methoxy oxide (II) structure.

On reacting an aqueous-alcoholic solution of semicarbazide acetate with methyl lactolide (II), a crystalline precipitate began to deposit after several hours; this was shown to be the semicarbazone of dimethylbenzoylcarbinol (III). On reacting an aqueous sulfuric acid solution of 2,4-dinitrophenylhydrazine with the methyl lactolide, the 2,4-dinitrophenylhydrazone of dimethylbenzoylcarbinol was obtained. Formation from the methyl

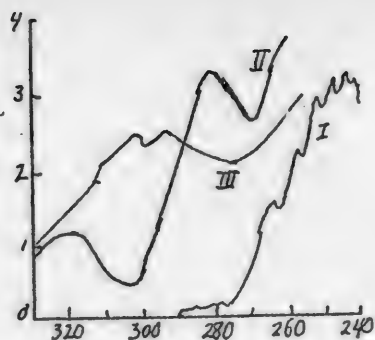


Fig. 1. I) Dimethylbenzoylcarbinol methyl lactolide; II) dimethylbenzoylcarbinol; III) methylphenylacetylcarbinol methyl ether.

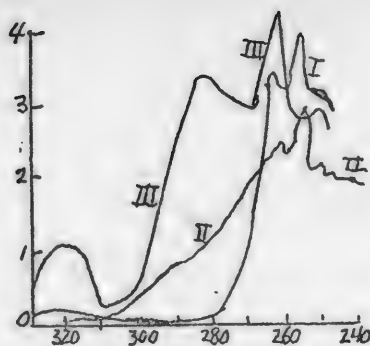


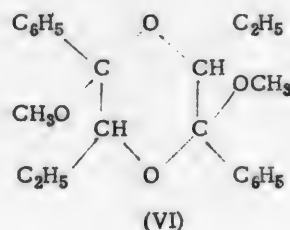
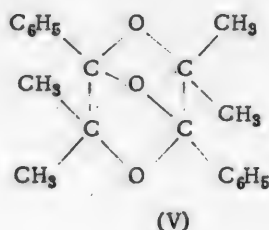
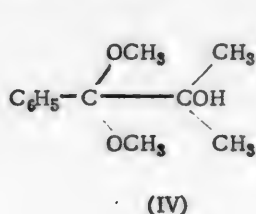
Fig. 2. I) Anhydrous dimethylbenzoylcarbinol dimer melting at 185-186°; II) ethylbenzoylcarbinol cyclodilactolide; III) dimethylbenzoylcarbinol oxalate ester.

lactolide of carbonyl group derivatives, corresponding to ketoalcohols, indicates the ease of hydrolyzing the methyl lactolides under study in acid aqueous solutions.

In connection with this, we should note that the reaction between α -bromo-isopropyl phenyl ketone and dry sodium methylate was performed by Aston, Clarke, Burgess, and Greenburg [2] in 1942. Based on the tendency of the substance to react with 2,4-dinitrophenylhydrazine with formation of a 2,4-dinitrophenylhydrazone, they incorrectly at-

tributed to it the formula of dimethylbenzoylcarbinol methyl ether. They did not analyze the dinitrophenyl hydrazone for its methoxy group content; the ease of methyl lactolide hydrolysis led the American authors into error. According to physical constants and melting point, the 2,4-dinitrophenylhydrazone of their substance is identical with the one we prepared.

By reacting methyl alcohol with dimethylbenzoylcarbinol methyl lactolide, we obtained dimethylbenzoylcarbinol dimethylketal (IV); this was shown by hydrolyzing the substance obtained to the ketoalcohol, and identifying the latter.

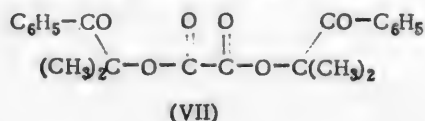


By reacting 2% HCl in absolute methyl alcohol or benzene with the methyl lactolide, a substance is formed which melts at 184-185°, together with a small quantity of ketoalcohol; this was previously obtained by A.E. Favorsky and N. Mandryka from dimethylbenzoylcarbinol on storage [3]. The structure of this substance has not been shown. It is probable that it is an anhydrocyclodilactal, and has structure (V). Assumptions with regard to the presence of a dioxane ring in the compound and its bicyclic structure are based on similarity of the absorption spectrum of this substance (Fig. 2., curve I) with the absorption spectrum of ethylbenzoylcarbinol cyclodimethyldilactolide (VI) (Fig. 2, curve II), in which there is no doubt about the presence of dioxane rings [4].

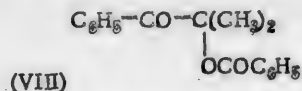
Assumptions on forming the anhydrous form of the dioxidioxane by reacting sodium bisulfate with ketals of α -ketoalcohols were discussed by I. N. Nazarov [5].

On reacting the methyl lactolide with oxalic acid in benzene, the oxide ring is broken on the side of the two methyl groups, and the full oxalate ester of dimethylbenzoylcarbinol (VII) is formed, whose structure was confirmed by hydrolysis and identification of the hydrolysis products.

The ultraviolet absorption spectrum also indicates presence in the substance of a benzoyl grouping (maxima at $\lambda = 322 \mu$, at 284μ , and at 262μ) (Fig. 2, curve III).

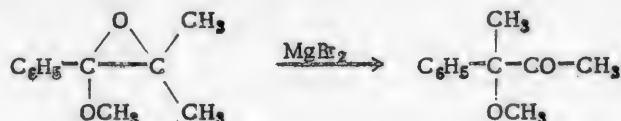


By reacting the methyl lactolide with benzoic acid in a benzene solution, the oxide ring is likewise readily opened, and a benzoic ester formed, evidently, of dimethylbenzoylcarbinol (VIII)



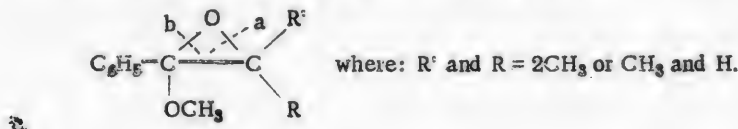
Conclusions on structure of this substance were drawn by analogy with oxalic acid esters where the ester structure was firmly established. Attempts to prepare the benzoic acid ester of dimethylbenzoylcarbinol by the usual method—by heating α -bromoisopropyl phenyl ketone with potassium benzoate in an alcohol solution—were unsuccessful; the bromoketone was recovered again in an unchanged form.

By comparing results of this study with data in the work by T. I. Temnikova and E. N. Kropacheva [6] on the relative action of acids on methyl lactolides (II) and (I), it can be seen that both methyl lactolides behave differently with regard to oxalic acid; whereas in reacting oxalic acid with dimethylbenzoylcarbinol methyl lactolide (II), ester formation occurs with oxide ring rupture on the side of the two methyl groups, in reacting oxalic acid with methylbenzoylcarbinol methyl lactolide, oxide ring rupture takes place on the phenyl side, and isomerization to phenylacetylcarbinol methyl ether was observed. We were able to cause isomeric transformation of dimethylbenzoylcarbinol methyl lactolide by action on it of magnesium bromide etherate in ether solution; here also oxide ring cleavage took place on the phenyl side with formation of methylphenylacetylcarbinol methyl ether:



The structure of the isomerization product was confirmed by oxidizing it with sodium hypobromite to methoxymethylphenylacetic acid, and also by spectrochemical methods. The absorption curve did not have a supplemental maximum in the λ region of 320 m μ , the maximum for the carbonyl group, as does phenylacetylcarbinol methyl ether, which shifts in the direction of longer waves (compare Fig. 1 of this work with Fig. 2 of reference [6]).

Thus, dimethylbenzoylcarbinol methyl lactolide is characterized by greater stability toward polymerization as compared with methylbenzoylcarbinol methyl lactolide, but shows a higher tendency toward oxide ring cleavage on hydrolysis and on reaction with various reagents; the order of this ring cleavage is the same—in forming esters of organic acids cleavage takes place on the side of the methyl groups (a); on action of sodium methylate and in isomerization, on the phenyl and methoxy group side (b):



EXPERIMENTAL

Preparation of dimethylbenzoylcarbinol methyl lactolide

A solution of 70 g bromoisopropylphenyl ketone in 100 ml absolute ether was added dropwise to a suspension of sodium methylate (from 10 g metallic Na) in 200 ml absolute ether with vigorous agitation. To obtain optimum yield (about 95%), the sodium methylate must be absolutely dry and finely pulverized. Reaction is completed in 7-10 hours. The ether solution was filtered from the mixture of NaBr and CH_3ONa ; following distillation of the ether, the residue was distilled in vacuum. B.p. 85-85.5° at 9.5 mm, 75-75.5° at 5 mm.

d_4^{17} 1.0124; n_D^{22} 1.49259; n_D^{25} 1.49583; n_D^{27} 1.50633; MR_α 51.09; MR_β 52.29. $\text{C}_{12}\text{H}_{14}\text{O}_2$.
Calculated: MR_α 50.52; MR_β 51.65.

0.1247 g substance: 0.3375 g CO_2 ; 0.0894 g H_2O . 0.1208 g substance: 0.3274 g CO_2 ; 0.0872 g H_2O .
0.1923 g substance: 0.2510 g AgI. Found %: C 73.81, 73.91; H 8.02, 8.07; CH_3O 17.2.

$\text{C}_{12}\text{H}_{14}\text{O}_2$. Calculated %: C 74.16; H 7.90; OCH_3 17.4.

* In calculating 0.35 was added per oxide ring increment for the α -line, and 0.45 for the β -line.

Reaction of the methyl lactolide with semicarbazide. A water-alcohol solution of semicarbazide acetate (from 1 g semicarbazide hydrochloride) was added to 1 g of the substance. The crystals separating in 24 hours were filtered and recrystallized from alcohol. M.p. 181-182°. The semicarbazone of dimethylbenzoylcarbinol melts at the same temperature. Mixture tests melted at the same temperature.

Reaction of the methyl lactolide with 2,4-dinitrophenylhydrazine. To 0.5 g of the substance dissolved in 20 ml alcohol was added a solution of 0.4 g dinitrophenylhydrazine and 2 ml H_2SO_4 in 3 ml water and 10 ml ethyl alcohol. The solution was allowed to stand overnight. The crystals which precipitated were separated, washed with alcohol, dried, and recrystallized from ligroin. M.p. 139-140°. The substance did not contain methoxy groups (determined by the Tseizel method).

0.1020 g substance: 14.4 ml N_2 (18°, 755.6 mm). 0.0859 g substance: 12.2 ml N_2 (18°, 755.3 mm).
Found %: N 16.35, 16.44. $C_{16}H_{15}O_5N_3$. Calculated %: N 16.28.

Hydrolysis of the methyl lactolide. 5 g of the substance was heated on a boiling water bath with vigorous agitation for a 6 hour period with 100 ml of aqueous 5% sulfuric acid. On cooling, the oil was extracted with ether, dried with $MgSO_4$, and the hydrolysis products distilled.

B.p. 128-129° at 12 mm; semicarbazone, m.p. 181-182°.

Found %: N 18.8. $C_{12}H_{15}O_2N_3$. Calculated %: N 19.01.

A glycol was obtained by reaction with magnesium phenyl bromide: 2-methyl-1,1-diphenylpropandiol-1,2 with a m.p. of 88-89°.

According to literature data, dimethylbenzoylcarbinol has a b.p. of 115-116° at 7 mm; semicarbazone m.p. 188° [7], 177-178° [8]; 2-methyl-1,1-diphenylpropandiol-1,2 m.p. 88-89° [9].

Reaction of dimethylbenzoylcarbinol methyl lactolide with methyl alcohol. 5 g of the methyl lactolide was dissolved in 50 ml methyl alcohol and allowed to stand for two days. After distilling the methyl alcohol under vacuum, an oily substance and crystals remained. The liquid portion was shown to be a mixture of substances. The crystals after recrystallization from light petroleum ether melted at 54-55°. Yield 1 g.

0.1195 g substance: 0.2997 g CO_2 ; 0.0932 g H_2O . 0.1036 g substance: 0.2595 g CO_2 ; 0.0816 g H_2O .
Methoxyl determination according to Fiebk: 0.0436 g substance: 24.7 ml 0.1 N $Na_2S_2O_3$. 0.0395 g substance: 22.5 ml 0.1 N $Na_2S_2O_3$. 0.1136 g substance: 11.9 ml CH_4 (13°, 756 mm). 0.1025 g substance: 10.8 ml CH_4 (13°, 756 mm). Found %: C 68.43, 68.36; H 8.73, 8.81; OCH_3 29.36, 29.45; number of active hydrogens 0.96, 0.97. $C_{12}H_{15}O_3$. Calculated %: C 68.57; H 8.57; OCH_3 29.52; number of active hydrogens 1.

Hydrolysis of the substance obtained, which appeared to be a ketal of dimethylbenzoylcarbinol, was performed by heating it on a water bath with 5% H_2SO_4 in water for a 1 hour period. Dimethylbenzoylcarbinol was identified as its semicarbazone with a m.p. of 181-182°.

Action of 1% HCl in benzene on dimethylbenzoylcarbinol methyl lactolide 4 g methyl lactolide was added dropwise to 50 ml dry benzene containing 1% HCl. The reaction takes place with warming. After 12 hours, the benzene solution was washed with water and soda solution and dried with $MgSO_4$. After removing the benzene in a vacuum, an oil was obtained which gave a positive reaction for halogens and contained dimethylbenzoylcarbinol. The crystalline substance was recrystallized from a mixture of alcohol and benzene; m.p. 185-186°. Found %: C 77.37; H 7.11. $C_{22}H_{25}O_3$. Calculated %: C 77.40; H 7.09

From the action of 1% HCl in absolute methyl alcohol there was similarly obtained dimethylbenzoylcarbinol and the substance with a 185-186° m.p.

Reaction of dimethylbenzoylcarbinol methyl lactolide with oxalic acid in benzene solution. 10 g methyl lactolide was added dropwise to 2 g anhydrous oxalic acid suspended in 34 ml dry benzene. The reaction mixture was allowed to stand for 24 hours, during the course of which the oxalic acid gradually went into solution. On the next day, the benzene solution was washed with an aqueous soda solution and dried over $MgSO_4$. After distilling the benzene under vacuum, a yellow liquid and colorless crystals remained as a residue. The crystals were separated from the liquid by filtration. The crystals were recrystallized from ethanol; m.p. 136°. (5 g).

0.1096 g substance: 0.2790 g CO_2 ; 0.0554 g H_2O . 0.1141 g substance: 0.2902 g CO_2 ; 0.0591 g H_2O .
The substance did not contain either OH or OCH_3 groups.
Found %: C 69.43, 69.36; H 5.66, 5.80. $C_{22}H_{25}O_6$. Calculated %: C 69.11; H 5.76.

Hydrolysis of the oxalate ester was performed by heating with aqueous alcoholic potassium hydroxide solution for a 5 hour period on a water bath. The ethyl alcohol was distilled under vacuum and the residue subjected to

ether extraction. Dimethylbenzoylcarbinol was separated from the neutral products, identified by its absorption spectrum in the ultraviolet and by its semicarbazone, which melted at 180-181°. No depression of melting point was observed with the semicarbazone of dimethylbenzoylcarbinol. Oxalic acid was separated via its calcium salt and acidification. After two recrystallizations from water and drying, the acid had m.p. 189° in a sealed capillary. The melting point of a mixture with commercial oxalic acid was the same. The calcium salt was prepared.

Reaction of dimethylbenzoylcarbinol methyl lactolide with benzoic acid. 3 g of the methyl lactolide was added to 3 g benzoic acid dissolved in 50 ml benzene. The solution was allowed to stand overnight, and then washed with an aqueous soda solution and dried over MgSO_4 . After distilling the benzene, colorless crystals remained, which after two recrystallizations from light petroleum ether melted at 61.5-62.5°.

0.1037 g substance: 0.2885 g CO_2 ; 0.0535 g H_2O . 0.1123 g substance: 0.3138 g CO_2 ; 0.0607 g H_2O .
Found %: C 75.93, 76.22; H 5.74 6.05. $\text{C}_{12}\text{H}_{16}\text{O}_3$. Calculated %: C 76.12; H 5.97.

Isomerization of dimethylbenzoylcarbinol methyl lactolide into methylphenylacetylcarbinol methyl ether. Isomerization was conducted with magnesium bromide etherate, prepared according to B. N. Menshutkin [10]. 7 g bromine was added to 1.5 g Mg under a layer of 10 ml absolute ether with strong agitation and cooling; the solution was then heated. After a little while two layers appeared in the flask: the upper one of ether and the lower one, an ether complex of magnesium bromide. 5 g dimethylbenzoylcarbinol methyl lactolide was then added dropwise to the flask and the solution agitated for a 5 hour period. The ether solution was washed with dilute hydrochloric acid and then with alkali, and dried with MgSO_4 . As a result of distillation at 3 mm, two fractions were obtained; 2.5 g at 85-86°, and 2 g at 86-89°. After a second distillation a narrow fraction was separated boiling at 86-86.5° at 3 mm.

d_4^{15} 1.037; n_D^{15} 1.49694. MR_α 50.34. $\text{C}_{11}\text{H}_{14}\text{O}_2$. Calculated MR_α 50.63.

0.1234 g substance: 0.3340 g CO_2 ; 0.0906 g H_2O . 0.1258 g substance: 0.3415 g CO_2 ; 0.0883 g H_2O .
0.0437 g substance: 14.35 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. Found %: C 73.81, 74.05; H 8.22, 7.86; OCH_3 16.98.
 $\text{C}_{11}\text{H}_{14}\text{O}_2$. Calculated %: C 74.16; H 7.90; OCH_3 17.40.

The semicarbazone was obtained by the usual method. After recrystallization from alcohol it melted at 154°.

0.1023 g substance: 15.3 ml N_2 (15°, 733 mm). 0.0983 g substance: 14.9 ml N_2 (16°, 733 mm).
Found %: N 18.01, 18.21. $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3$. Calculated %: N 17.87.

Methoxyketone oxidation. Oxidation was performed by sodium hypobromite prepared from 2.7 g of NaOH and 4 g bromine. 1.5 g ketone was added dropwise to the hypobromite solution at 20° with constant agitation; heavy droplets began to collect at the bottom of the flask after 30 minutes. Reaction continued for 3 hours. Bromoform was separated and was distilled after drying. B.p. 151-152°; n_D^{15} 1.609 (according to the literature data, b.p. 150.5°, n_D^{15} 1.598).

The alkaline solution was extracted with ether to remove neutral products, and then dried and acidified with hydrochloric acid. The oil separated was extracted with ether and dried over MgSO_4 . The acid was precipitated as its ammonium salt from the ether solution, using dry NH_3 . The ammonium salt was a white colored crystalline solid, soluble in water; by reacting it with AgNO_3 solution, the silver salt of the acid was separated; this was used for analysis.

0.1410 g substance: 0.2150 g CO_2 ; 0.0515 g H_2O . 0.0530 g Ag. 0.1462 g substance: 0.2252 g CO_2 ; 0.0530 g H_2O ; 0.0551 g Ag. 0.0786 g substance: 15.7 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. Found %: C 41.60, 41.99. H 4.09, 4.05; Ag 37.61, 37.70; OCH_3 10.33. $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Ag}$. Calculated %: C 41.81; H 3.83; Ag 37.63; OCH_3 10.80.

SUMMARY

1. Dimethylbenzoylcarbinol methyl lactolide (1-methoxy-1-phenyl-2,2-dimethylethylene oxide) is obtained by reacting sodium methylate in absolute ether with α -bromoisopropyl phenyl ketone. The methyl lactolide was stable and did not polymerize on storage, but was readily hydrolyzed in aqueous acid solutions with formation of dimethylbenzoylcarbinol; because of this the corresponding ketoalcohol derivative was obtained on reacting the methyl lactolide with semicarbazide or 2,4-dinitrophenylhydrazine.

2. The dimethylketal of dimethylbenzoylcarbinol is formed by reacting the methyl lactolide with methyl alcohol.

3. On reacting the methyl lactolide with benzoic or oxalic acids, corresponding esters of dimethylbenzoyl carbinol are formed.

4. Under action of magnesium bromide etherate, the methyl lactolide undergoes isomerization and methyl-phenylacetylcarbinol methyl ether is obtained.

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Received September 9, 1952

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* See Consultants Bureau Translation, p. a-541.

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THE PROBLEM OF FORMING DERIVATIVES OF β -IMINODIACRYLIC ACIDS

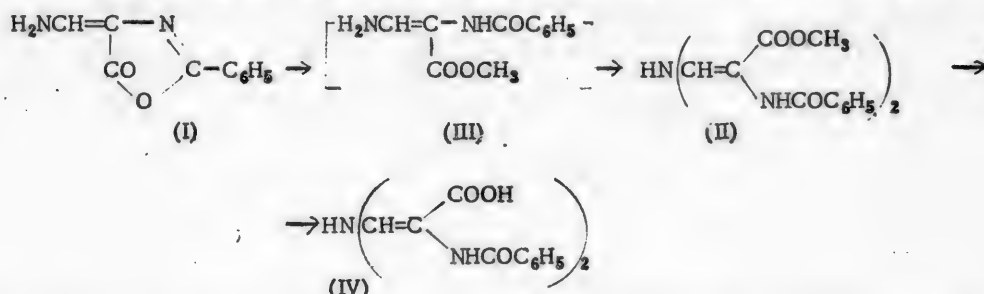
I. T. Strukov

In studying chemical properties of certain α -substituted β -aminoacrylic acids, it was found that they could be rather readily transformed into derivatives of β -aminodiacrylic acids.

A similar reaction was described by M. V. Rubtsov [1]. By heating the ethyl ester of β -*p*-anisidineacrylic acid in a vacuum at 100°, M. V. Rubtsov obtained the ethyl ester of β -*p*-anisidinediacrylic acid and *p*-anisidine.

The author has shown [2] that in ether solution in presence of hydrogen chloride the methyl ester of α -phenyl- β -aminoacrylic acid changes to the methyl ester of β -iminodi-(α -phenylacrylic acid). On saponifying the ester with an alcoholic potassium hydroxide solution, the potassium salt of β -iminodi-(α -phenylacrylic acid) was obtained, and the free acid prepared from it.

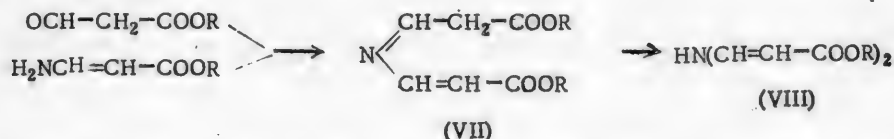
In the present paper we describe another similar transformation reaction. By action of a hydrogen chloride solution in methyl alcohol on 4-aminomethylene-2-phenyl-5-oxazolone (I), the methyl ester of β -iminodi-(α -benzoylaminoacrylic acid) (II) slowly forms. Evidently, the reaction is via a stage of forming the methyl ester of α -benzoylamido- β -aminoacrylic acid (III). By saponifying ester (II) with potassium hydroxide solution, the potassium salt of the acid was formed, and then the free β -iminodi-(α -benzoylamidoacrylic acid) (IV):



To explain the reaction mechanism, it is necessary to make several very probable assumptions. Esters of β -aminoacrylic acid exist in two tautomeric forms (V) and (VI):



The presence of hydrogen chloride will promote transformation of the β -aminoacrylic acid ester (V) into the aldimine form (VI), and presence of traces of water, always present in alcohol or ether, leads to decomposition of the molecule into ammonium chloride and a β -oxopropionic acid ester. Subsequently, the β -oxopropionic acid ester enters into reaction with an as-yet-unchanged molecule of β -aminoacrylic acid ester; here the water separated takes up hydrogen chloride, and the tautomeric form (VII) is obtained, which changes into a β -iminodiacrylic acid ester (VIII):



Thus, a small quantity of water can promote almost complete transformation of a β -aminoacrylic acid ester into a β -iminodiacrylic acid ester. This was shown by transforming (I) into (II); the yield of β -iminodi-(α -benzoylamidoacrylic acid) methyl ester reached 90%.

In presence of hydrogen chloride, this reaction goes without consumption of external energy, while heating is necessary to convert the ethyl ester of β -*p*-anisidineacrylic acid into the ethyl ester of β -*p*-anisidinediacrylic acid.

We may assume that formation of β -iminodiacrylic acid esters and their derivatives takes place by a scheme which may be considered as a general one for the given series of compounds.

EXPERIMENTAL

β -Iminodi-(α -phenylacrylic acid)

1 g β -iminodi-(α -phenylacrylic acid) methyl ester was heated with 10 ml 10% potassium hydroxide solution in methyl alcohol for a 24 hour period at 50-55°. The white crystalline precipitate which separated was filtered, washed with methyl alcohol, and dissolved in 50 ml water. The solution was treated with 0.5 g charcoal at 15-20° and filtered. On acidification of the filtrate, a pale yellow substance separated which, after recrystallization from methyl alcohol, melted at 168-170° (with decomposition).

7.374 mg substance: 0.300 ml N_2 (21°, 721 mm). 7.673 mg substance: 0.307 ml N_2 (21°, 721 mm).

0.0206 g substance: 1.31 ml 0.1 N NaOH. Found %: N 4.48, 4.46; COOH 28.59.

$C_{12}H_{15}O_4N$. Calculated %: N 4.53; COOH 29.12.

Methyl ester of β -iminodi-(α -benzoylamidoacrylic acid) (II)

25 ml methyl alcohol was saturated with 5 g dry hydrogen chloride. 4 g 4-aminomethylene-2-phenyl-5-oxazolone was added to the solution and allowed to stand for 5 days at 18-20°. The azlactone gradually went into solution, and a crystalline precipitate simultaneously separated in the form of long, pale-yellow, silky needles. The residue was filtered (4 g) and recrystallized from methyl alcohol. M.p. 230-231° (with decomposition).

4.945 mg substance: 0.466 ml N_2 (25°, 737.5 mm). 4.115 mg substance: 0.373 ml N_2 (23°, 739 mm).

5.692 mg substance: 8.31 ml 0.02 N $Na_2S_2O_3$. 5.097 mg substance: 7.39 ml 0.02 N $Na_2S_2O_3$.

Found %: N 10.02, 10.16; OCH_3 15.09, 15.00. $C_{22}H_{21}O_6N_3$. Calculated %: N 9.95; OCH_3 14.62.

β -Iminodi-(α -benzoylamidoacrylic acid) (IV)

1 g of β -iminodi-(α -benzoylamidoacrylic acid) methyl ester was heated with 10 ml 10% potassium hydroxide solution in methyl alcohol. The substance dissolved and then a precipitate separated, which went into solution on addition of 20 ml water. A yellow crystalline substance separated on acidification of the solution with hydrochloric acid. It was recrystallized from methyl alcohol, m.p. 165-166°.

3.116 mg substance: 6.929 mg CO_2 ; 1.271 mg H_2O . 3.768 mg substance: 8.422 mg CO_2 ; 1.428 mg H_2O .

4.701 mg substance: 3.61 ml 0.01 N H_2SO_4 . 5.898 mg substance: 6.538 ml N_2 :

(23.5°, 749 mm). Found %: C 60.68, 60.0. H 4.56, 4.41. N 10.75, 10.53. $C_{20}H_{17}O_6N_3$. Calculated %: C 60.78; H 4.34; N 10.63.

SUMMARY

1. The transformation of β -amino- α -benzoylamidoacrylic acid methyl ester into β -iminodi-(α -benzoylamidoacrylic acid) methyl ester is shown.

2. Assumptions are discussed with regard to reaction mechanism for forming esters of β -iminodiacrylic acids and their derivatives from the corresponding β -aminoacrylic acid esters.

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Received August 21, 1952.

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* See Consultants Bureau Translation, p. 1657.

SYNTHESIS AND TRANSFORMATION OF β -(DIETHYLAMINO)ETHYLMETHYLVINYLETHINYLCARBINOL

A. G. Terzyan

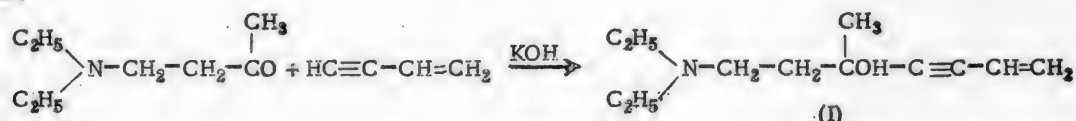
The condensation of carbonyl compounds with singly substituted acetylenic hydrocarbons, discovered and studied by A. E. Favorsky [1], has had wide application as a most general method for preparing acetylenic alcohols and glycols. This reaction (in its various variations) continues to have wide development even at the present time. In particular, I. N. Nazarov and his coworkers have studied in detail the reaction of condensing acetylenic hydrocarbons with aminoketones of the piperidine series [2].

The similar condensation of vinylacetylene or its homologs with aliphatic aminoketones has not been reported previously.

It was shown in a previous paper [3] that on condensing vinylacetylene with β -dimethylaminobutanone in presence of powdered potassium hydroxide, aminoalcohols of the vinylacetylene series are formed, from which saturated and unsaturated amines, as well as the corresponding aminoalcohols, were obtained by dehydration and catalytic hydrogenation.

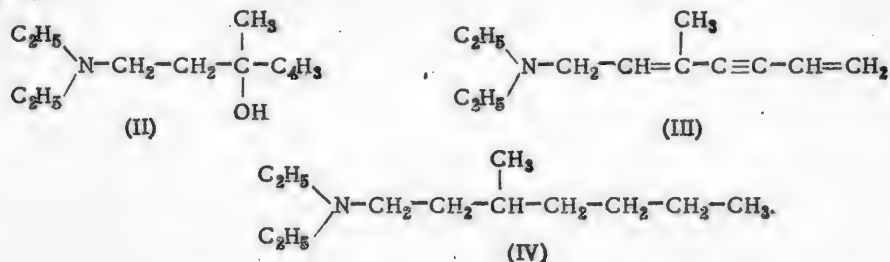
The present paper is concerned with synthesis of a second example of this aminoalcohol series — β -(diethylamino)-ethylmethylvinylethynylcarbinol (I), and also to describe the products of its corresponding transformations.

The aminoalcohol (I) was obtained with a 70.9% yield by condensing vinylacetylene with β -diethylaminobutanone:



Catalytic hydrogenation of aminoalcohol (I) was performed in ethyl alcohol in presence of platinum black. The corresponding saturated aminoalcohol — 1-diethylamino-3-methylheptanol-3 (II) — was obtained with a 73% yield.

By dehydrating the starting aminoalcohol (I) with sulfuric acid, we obtained an amine of the divinylacetylene series; its structure could be expressed by formula (III) by analogy with previously prepared and studied homologs, [3].



By catalytic hydrogenation of amine (III), we obtained the corresponding saturated amine (IV), which was formed with a yield of 77% of the theoretical quantity.

EXPERIMENTAL

β -(Diethylamino)ethylmethylvinylethynylcarbinol (I)

A solution of 21.3 g of β -diethylaminobutanone and 20 ml vinylacetylene in 25 ml dry ether was added in small portions with continued shaking and cooling in an ice-salt mixture during a 4 hour period to a mixture of 12 g powdered potassium hydroxide in 40 ml dry ether. The reaction mixture was stirred for 4 hours with cooling in ice water, and for 3 hours at room temperature. On the following day, the ethereal solution of reaction

products was washed with water and dried over sodium sulfate. After removing the ether, the residue was vacuum distilled. 20.6 g (70.91% of the theoretical quantity) of a colorless oily substance was obtained, with b.p. 123-125° at 22 mm.

d_4^{20} 0.9020; n_D^{20} 1.4800; found: MR_D 61.53. $C_{12}H_{23}ON$. Calculated MR_D 60.73.

0.1022 g substance: 0.2762 g CO_2 ; 0.1016 g H_2O . Found %: C 73.70; H 11.04. $C_{12}H_{23}ON$. Calculated %: C 73.84; H 10.76. 0.0658 g substance: 6.6 ml 0.05 N H_2SO_4 . 0.0586 g substance: 6.99 ml 0.05 N H_2SO_4 . Found: M 199, 195.1. $C_{12}H_{23}ON$. Calculated: M 195. 0.0636 g substance: 12.8 ml CH_4 (26.5°, 678 mm). 0.0586 g substance: 12.0 ml CH_4 (31°, 674 mm). Found OH groups: 1. $C_{12}H_{23}ON$. Calculated OH groups: 1.

1-Diethylamino-3-methylheptanol-3 (II).

6.65 g freshly distilled carbinol (I) was hydrogenated in 20 ml ethyl alcohol with platinum black. Hydrogenation was rapid at first, and slowed down at the end. 2.29 liters of hydrogen is required for complete reduction; 2.27 liters was absorbed. 5.03 g (73.51% of the theoretical quantity) of 1-diethylamino-3-methylheptanol-3 (II) was obtained, with b.p. 108° at 20 mm; a mobile liquid with a specific amine odor.

d_4^{20} 0.8562; n_D^{20} 1.4487; found: MR_D 62.87. $C_{12}H_{27}ON$. Calculated MR_D 63.20.

0.0936 g substance: 4.7 ml 0.1 N H_2SO_4 . Found: M 198.2. $C_{12}H_{27}ON$. Calculated M 201.

0.0938 g substance: 0.2472 g CO_2 ; 0.1264 g H_2O . Found %: C 71.87; H 13.78. $C_{12}H_{27}ON$. Calculated %: C 71.64; H 13.43. 0.0640 g substance: 17 ml CH_4 (22°, 680 mm). Found: OH groups: 1.

$C_{12}H_{27}ON$. Calculated OH groups: 1.

Its hydrogen chloride salt, obtained by passing a stream of dry hydrogen chloride through an ether solution of the amine, was a hygroscopic amorphous white powder, which came out as a viscous, non-crystallizing mass on attempts to crystallize it.

0.1103 g substance: 0.0686 g AgCl. Found %: Cl 15.39. $C_{12}H_{28}ONCl$. Calculated %: Cl 14.95.

1-Diethylamino-3-methylheptadiene-2,6-yne-4 (III).

138 ml concentrated sulfuric acid was added slowly while continually stirring and cooling in ice water to a mixture of 115 g carbinol (I) and 64 ml water. After stirring for a 20 hour period on a water bath at a temperature of 60-70°, a small quantity of water was added and the mixture neutralized with potassium acetate while cooling with ice. After removing the ether layer, the water layer was washed with ether; the ether solution was dried with sodium sulfate and the solvent distilled. On distilling the remaining oil 78 g (74.71% of the theoretical quantity) of a pale yellow liquid was obtained, having an amine odor, and boiling at 91-92° at 9 mm.

d_4^{20} 0.8896; n_D^{20} 1.5058; found MR_D 59.47. $C_{12}H_{19}N$. Calculated MR_D 58.62.

0.0308 g substance: 3.36 ml 0.05 N H_2SO_4 . Found M 179.1. $C_{12}H_{19}N$. Calculated: M 177. 0.0865 g substance: 7.2 ml N_2 (24°, 679 mm). Found %: N 8.19. $C_{12}H_{19}N$. Calculated %: N 7.91.

The compound obtained should be analogous in structure with the product from dehydrating β -(dimethylamino)ethylmethylvinylethynylcarbinol = 1-dimethylamino-3-methylheptadiene-2,6-yne-4. The structure of this substance was established earlier [3] by oxidizing it with potassium permanganate to dimethylaminoacetic acid, identified via its hydrogen chloride salt.

1-Diethylamino-3-methylheptane (IV)

2.7 g freshly distilled aminodienyne (III) was hydrogenated in 20 ml alcohol over a platinum catalyst. 1.36 liters of hydrogen is required for complete reduction; 1.3 liters was absorbed. The catalyst was filtered, alcohol distilled, and the product distilled under vacuum. 2.2 g amine (IV) (77.3% of the theoretical quantity) was obtained as a mobile liquid, boiling at 80-82° at 11 mm.

d_4^{20} 0.8172; n_D^{20} 1.4610; found: MR_D 62.11. $C_{12}H_{27}N$. Calculated: MR_D 61.56.

0.0472 g substance: 2.6 ml 0.1 N H_2SO_4 . Found: M 181.7. $C_{12}H_{27}N$. Calculated M: 185.

0.1304 g substance: 9.4 ml N_2 (23°, 680 mm). Found %: N 7.43. $C_{12}H_{27}N$. Calculated %: N 7.56.

The hydrogen chloride salt of this amine was a hygroscopic, amorphous white powder, which decomposed on storage in air, and came out in the form of a viscous noncrystallizing mass on attempts to recrystallize it.

SUMMARY

1. It was shown that β -(diethylamino)ethylmethylvinylethynylcarbinol, obtained by condensing β -diethylaminobutanone with vinylacetylene, forms the corresponding saturated carbinol on catalytic hydrogenation.

2. By reacting with sulfuric acid, β -(diethylamino)ethyl-methylvinylethynylcarbinol is dehydrated to the corresponding aminodienyne. The corresponding aminoheptane is obtained by hydrogenation of the latter.

3. The following were obtained for the first time and described: β -(diethylamino)ethylmethylvinylethynylcarbinol, 1-diethylamino-3-methylheptadiene-2,6-yne-4, 1-diethylamino-3-methylheptanol-3, and 1-diethylamino-3-methylheptane.

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Received March 21, 1953

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RESEARCH IN THE FIELD OF ALKANOSULFONIC ACIDS

X. METHYLATION OF THE N-ARYLAMIDES OF ALKANOSULFONIC ACIDS

A. G. Kostsova

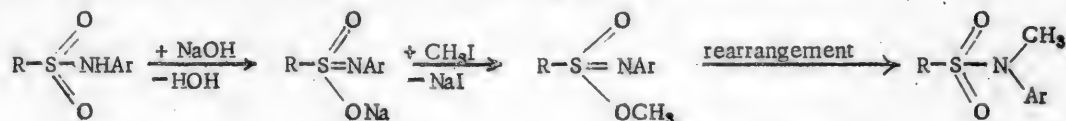
N-Arylamides of alkanosulfonic acids, having the general formula RSO_2NHAr , contain in their composition the NH group with a mobile hydrogen atom, which can be replaced by various radicals, for example, alkyl, acyl, and others. Nevertheless, the alkylation and acylation reactions of the N-arylamides of alkanosulfonic acids have been studied very little [1]. The reactions mentioned have been described with relative completeness in the literature only for the p-phenetide of ethanesulfonic acid [2]. Directions for alkylation of N-arylamides of disulfonic acids are present in the literature [3, 4].

Alkylation is usually carried out in an alkaline medium, with alkyl halides, alkyl sulfates, diazomethane, and other reagents playing the role of alkylating agents.

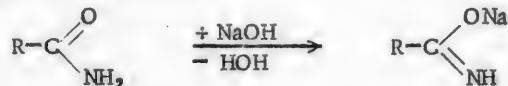
The purpose of the present work was to study the methylation of anilides, p-anisidides, and certain p-phenetides of alkanosulfonic acids synthesized by the author. The author used methyl iodide as the methylating agent. Methylation was carried out in an alkaline medium. The methylation products separated readily from the reaction mixture, due to complete insolubility in alkali. This property readily distinguishes them from the initial N-arylsulfonamide, which, in contrast, dissolves readily in alkalies. Attempts to carry out methylation without alkalies, in the presence of absolute ether medium, as well as in the absence of solvent, by direct interaction of N-arylsulfonamides with methyl iodide, led to negative results. In both cases unchanged N-arylsulfonamides were isolated.

These experiments indicated that methylation of the latter proceeds under strictly defined conditions, notably, only in an alkaline medium. On the other hand, the point should be stressed that N-arylsulfonamides, as the author's observations have shown, possess a neutral character; this is demonstrated by the neutral reaction to litmus, and also by the pH value, which fluctuates from 6 to 7.

However, as neutral compounds they dissolve readily in alkalies, in a manner analogous to primary and secondary nitro compounds, i.e., they behave as typical pseudo acids. Hence, proceeding from the fact that N-arylsulfonamides do not alkylate without alkalies, the author advances the assumption that they isomerize to the aci-form under the action of alkalies, and in this form they methylate, the resulting O-methyl derivative then regrouping into the N-methyl derivative according to the following equation:



Such an isomerization is possible, considering also the analogy to amides of the carboxylic acids, which are inclined toward similar tautomeric transformations. Therefore, for some of their metallic derivatives, a structure can be attributed, corresponding to the tautomeric form



The methylated N-arylamides of the alkanosulfonic acids obtained by the author were colorless, crystalline substances, readily soluble in alcohol, insoluble in ether, and stable to water hydrolysis; for example, they remained unchanged after 10 hours of boiling with water.

EXPERIMENTAL

The anilides, p-anisidides, and p-phenetides required for methylation were synthesized by the method described in the preceding works [5] of the author. 7-8% alkali was used to dissolve the N-arylsulfonamides. Methyl iodide was taken in four times the amount calculated according to the equation. Methylation procedure

No.	Formula	Name	M.p. (°C)	Quantity of initial substance taken (g)		Yield of product (%)	Analytical data for N (%)		Empirical formula
				N-aryl-sulfonamide*	Methyl iodide		Found	Calc.	
1	$\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$	Methanesulfonyl-N-methylanilide	78°	0.6	2.0	59	7.48	7.57	$\text{C}_8\text{H}_{11}\text{O}_2\text{NS}$
2	$\text{CH}_3\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$	Ethanesulfonyl-N-methylanilide	65	0.5	1.5	40	7.06	7.03	$\text{C}_9\text{H}_{13}\text{O}_2\text{NS}$
3	$(\text{CH}_3)_2\text{CHSO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$	2-Methylethanesulfonyl-N-methylanilide	55	0.4	1.12	38	6.52	6.57	$\text{C}_{10}\text{H}_{15}\text{O}_2\text{NS}$
4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$	Butanesulfonyl-N-methylanilide	54	1.8	5.2	62.5	6.13	6.16	$\text{C}_{11}\text{H}_{17}\text{O}_2\text{NS}$
5	$(\text{CH}_3)_2\text{CHCH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$	2-Methylpropanesulfonyl-N-methylanilide	72	0.5	1.3	34	6.07	6.16	$\text{C}_{11}\text{H}_{17}\text{O}_2\text{NS}$
6	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$	2-Methylbutanesulfonyl-N-methylanilide	81	0.35	0.80	40	5.57	5.80	$\text{C}_{12}\text{H}_{19}\text{O}_2\text{NS}$
7	$\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3$	Methanesulfonyl-N-methyl-p-aniside	69	0.6	1.78	36	6.42	6.51	$\text{C}_9\text{H}_{13}\text{O}_3\text{NS}$
8	$\text{CH}_3\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3$	Ethanesulfonyl-N-methyl-p-aniside	20(?)	0.4	1.0	—	—	—	$\text{C}_{10}\text{H}_{15}\text{O}_3\text{NS}$
9	$(\text{CH}_3)_2\text{CHSO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3$	2-Methylethanesulfonyl-N-methyl-p-aniside	56	0.35	0.80	43.2	5.72	5.76	$\text{C}_{11}\text{H}_{17}\text{O}_3\text{NS}$
10	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3$ **	Butanesulfonyl-N-methyl-p-aniside	45	0.31	0.8	78.7	5.10	5.44	$\text{C}_{12}\text{H}_{19}\text{O}_3\text{NS}$
11	$(\text{CH}_3)_2\text{CHCH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3$	2-Methylpropanesulfonyl-N-methyl-p-aniside	53	0.6	0.7	35	5.30	5.44	$\text{C}_{12}\text{H}_{19}\text{O}_3\text{NS}$
12	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3$...	2-Methylbutanesulfonyl-N-methyl-p-aniside	55	0.35	0.8	44.4	5.06	5.16	$\text{C}_{13}\text{H}_{21}\text{O}_3\text{NS}$
13	$(\text{CH}_3)_2\text{CHSO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$	2-Methylethanesulfonyl-N-methyl-p-phenetide	56	0.4	0.9	47.6	5.22	5.44	$\text{C}_{12}\text{H}_{19}\text{O}_3\text{NS}$
14	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$ **	2-Methylbutanesulfonyl-N-methyl-p-phenetide	65	0.4	0.8	71.4	4.51	4.91	$\text{C}_{12}\text{H}_{19}\text{O}_3\text{NS}$

* Initial N-arylsulfonamides: 1-6, anilides; 7-12, p-anisidides; 13-14 p-phenetidides.

** Butanesulfonyl-N-methyl-p-aniside obtained by L. D. Yakimova.

*** 2-Methylbutanesulfonyl-N-methyl-p-phenetide was obtained by V. D. Levitan

used by the author was the same for all of the N-arylsulfonamides; a general description is therefore given below, and specific data are given in the table only for the most characteristic experiments. Melting points for the synthesized methylated derivatives are also placed in the table.

The requisite quantity of N-arylsulfonamide was dissolved in a small volume of alkali (3-4 ml). A four-fold excess of methyl iodide was added to the alkaline solution, the mixture shaken vigorously, and the emulsion formed heated on a water bath at 40-45° with a reflux condenser for 1-1.5 hours. After termination of heating,

the mixture was left at room temperature until the following day. The contents of the reaction flask were then poured out onto a large watch glass or into a crystallizing dish for evaporation of the excess methyl iodide. As the latter evaporated, colorless crystals separated from the alkaline solution, which were separated from the alkalis, washed with water, dried and then recrystallized from a mixture of alcohol and water.

Upon methylating ethanesulfonyl-p-aniside, the reaction product separated from alkaline solution as an oil, which did not crystallize upon cooling, or upon prolonged rubbing with a glass rod. In such case the oil was carefully separated from the alkali, dissolved in a small amount of alcohol, and precipitated with water by cooling and rubbing with a glass rod. Crystals were isolated from the water-alcohol mixture, which softened at 9-10°. Attempt to separate by filtration resulted in conversion to an oily spot on the filter. Nevertheless, it was possible to isolate a very small amount of the crystals. The melting point was about 20°. It was not possible to analyze the product.

SUMMARY

1. The methylation reaction for the anilides, p-anisides and p-phenetides of alkane sulfonic acids has been studied.
2. The N-methylanilides and N-methyl-p-anisides of methane-, ethane-, 2-methylethane-, butane-, 2-methylpropane- and 2-methylbutane-sulfonic acids, and the N-methyl-p-phenetides of 2-methylethane and 2-methylbutane sulfonic acids have been synthesized and characterized for the first time.
3. It has been demonstrated that methylation proceeds only in an alkaline medium. Methylation does not proceed in absolute ether or in the absence of solvent.

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Received March 29, 1953

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* See Consultants Bureau Translation, p. 1471.



ORGANIC INSECTOFUNGICIDES

XIV. SYNTHESIS OF MIXED ESTERS OF DITHIOPHOSPHORIC ACID

N. N. Melnikov and K. D. Shvetsova-Shilovskaya

Mixed esters of phosphoric and thiophosphoric acids have acquired greater and greater importance in agriculture as a resource in the struggle against various plant pests, and their scale of application is continuously increasing [1-7]. A favorable property of this class of compounds is their rather universal character and rapidity of action upon various plant pests. Of interest in this respect are the esters of dithiophosphoric acid, which although somewhat less active than the mixed esters of thiophosphoric acid, are less dangerous to work with [8].

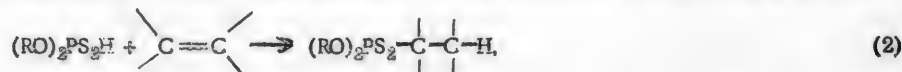
There are described in the literature only a limited number of methods for the synthesis of dithiophosphoric acid esters, the most important among them being the reaction of dialkyldithiophosphoric acid salts with halogen derivatives [9, 10].



By this method has been obtained a majority of the mixed esters of dithiophosphoric acid described up to the present time. However, this method produces good ester yields only in those cases where the halogen of the halogen derivatives is sufficiently mobile.

It was of interest to the authors to study the addition reaction of dialkyldithiophosphoric acid to the double bond of unsaturated compounds, and to clarify the possibility of synthesizing mixed esters of dithiophosphoric acid by such reaction. The addition of dialkylphosphorous acids to unsaturated compounds was achieved recently by A. N. Pudovik and B. A. Arbuzov [11-15].

As a result of experiments carried out at the start of 1951, it was possible to determine that the reaction of dialkyldithiophosphoric acid with unsaturated compounds will proceed according to the following scheme:



as the result of which quite satisfactory yields of dithiophosphoric acid esters have been produced. The reaction proceeds in the cold in the presence of small amounts of solid potassium hydroxide or other bases. The reaction of dialkyldithiophosphoric acid with unsaturated hydrocarbons proceeds according to the following general equation:



This reaction has been studied by the authors, using as an example the interaction of dialkyldithiophosphoric acids with styrene. The resulting compounds and their properties are given in Table 1.

It should be mentioned that after completion of the given work, there appeared directions in the literature for the synthesis of certain of the compounds [16] given in Table 1.

The interaction of dialkyldithiophosphoric acids with unsaturated compounds or with esters of the unsaturated alcohols proceeds according to scheme (4):



In this fashion allyl alcohol and vinyl acetate reacted. The compounds synthesized by the authors, and their properties, are given in Table 2.

The reaction of dialkyldithiophosphoric acids with unsaturated monobasic acids proceeds analogously (Scheme 5):



The compounds synthesized and their properties are given in Table 3.

TABLE 1

Mixed Esters of Dithiophosphoric Acid Obtained from Alcohols and Dialkylidithiophosphoric Acids

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(CH_3O)_2PS_2H$	$CH_2=CH-C_6H_5$	50	128-132	0.45	1.5705	1.2108	11.82	11.5/11.65
$(C_2H_5O)_2PS_2H$	$CH_2=CH-C_6H_5$	35	135-137	0.15	1.5498	1.1444	10.67	11.0/11.28
$(C_3H_7O)_2PS_2H$	$CH_2=CH-C_6H_5$	28	129-131	0.1	1.5381	1.0990	9.73	9.82/9.92
$(iso-C_3H_7O)_2PS_2H$	$CH_2=CH-C_6H_5$	38.5	121-124	0.2	1.5365	1.0966	9.73	9.81/9.95
$(C_4H_9O)_2PS_2H$	$CH_2=CH-C_6H_5$	13	137-140	0.025	1.5320	1.0890	8.94	8.82/8.8
$(iso-C_4H_9O)_2PS_2H$	$CH_2=CH-C_6H_5$	17.5	117-122	0.04	1.5301	1.0860	8.94	9.1/9.18

TABLE 2

Mixed Esters of Dithiophosphoric Acid Obtained by Interaction of Dithiophosphoric Acid with Unsaturated Alcohols and Esters

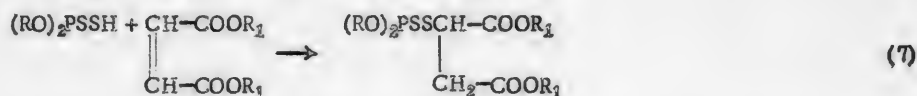
Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(CH_3O)_2PS_2H$	$CH_2=CHOCOCH_3$	38	100-103	2	1.5252	1.1558	12.63	13.3 13.4
$(C_2H_5O)_2PS_2H$	$CH_2=CHOCOCH_3$	71	115-117	1.5	1.4948	1.1517	11.4	11.37 11.34
$(C_3H_7O)_2PS_2H$	$CH_2=CHOCOCH_3$	46	80-81	0.05	1.5075	1.0984	10.32	9.90 9.92
$(iso-C_3H_7O)_2PS_2H$	$CH_2=CHOCOCH_3$	50	72-74	0.1	1.4335	1.0846	10.32	10.9 10.8
$(iso-C_4H_9O)_2PS_2H$	$CH_2=CHOCOCH_3$	43	104	0.075	1.4858	1.0926	9.43	9.96 10.1
$(C_4H_9O)_2PS_2H$	$CH_2=CHOCOCH_3$	25	109	0.4	1.4915	1.0915	9.43	10.22 10.48
$(C_4H_9O)_2PS_2H$	$CH_2=CHCH_2OH$	14.1	90-95	0.03	1.4835	1.0491	10.31	10.21 10.02

TABLE 3

Mixed Esters of Dithiophosphoric Acid Obtained from Dithiophosphoric Acids and the Esters of Unsaturated Acids

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(CH_3O)_2PS_2H$	$CH_2=CHCOOCH_3$	67	145	3	1.5160	1.2625	12.69	12.71 12.78
$(C_2H_5O)_2PS_2H$	$CH_2=CHCOOCH_3$	83	167	1.5	1.5050	1.1911	11.38	11.92 11.98
$(iso-C_4H_9O)_2PS_2H$	$CH_2=CHCOOCH_3$	58	124-129	0.2	1.4915	1.1172	9.43	9.62 9.72
$(CH_3O)_2PS_2H$	$CH_2=C(CH_3)COOCH_3$	38	133-135	2	1.5100	1.2330	12.01	12.01 12.0
$(C_2H_5O)_2PS_2H$	$CH_2=C(CH_3)COOCH_3$	59	154.5	5	1.4995	1.1577	10.82	11.31 11.35
$(iso-C_3H_7O)_2PS_2H$	$CH_2=C(CH_3)COOCH_3$	47	84-85	0.02	1.4935	1.1203	9.84	10.15 10.28
$(iso-C_4H_9O)_2PS_2H$	$CH_2=C(CH_3)COOCH_3$	56	115-116	0.04	1.4915	1.1138	9.05	9.32 9.16
$(C_4H_9O)_2PS_2H$	$CH_2=C(CH_3)COOCH_3$	38	110	0.025	1.4918	1.1132	9.05	8.8 9.14

Addition of dithiophosphoric acids to acrylonitrile and maleic acid esters proceeds quite easily. This reaction can be represented by schemes 6 and 7 :



The compounds obtained by the authors, with their properties, are given in Tables 4 and 5.

TABLE 4

Mixed Esters of Dithiophosphoric Acid Synthesized from Dialkyldithiophosphoric Acids and Acrylonitrile

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n _D ²⁰	d ₄ ²⁰	Phosphorus analysis	
							P calc'd (%)	P found (%)
(C ₂ H ₅ O) ₂ PS ₂ H	CH ₂ =CHCN	33	137-142	3.5	1.5195	1.1704	12.93	12.75 12.88
(C ₃ H ₇ O) ₂ PS ₂ H	CH ₂ =CHCN	30	116-120	0.05	1.5068	1.0505	11.59	11.98 11.71
(C ₄ H ₉ O) ₂ PS ₂ H	CH ₂ =CHCN	27.5	121-123	0.03	1.5050	1.0816	10.5	10.51 10.61
iso-(C ₄ H ₉ O) ₂ PS ₂ H	CH ₂ =CHCN	44	122-123	0.05	1.5010	1.0986	10.5	10.81 11.0
iso-(C ₃ H ₇ O) ₂ PS ₂ H	CH ₂ =CHCN	44.7	98-99	0.05	1.5020	1.0182	11.59	12.05 11.91

TABLE 5

Mixed Esters of Dithiophosphoric Acid Synthesized from Dialkyldithiophosphoric Acids and Esters of Maleic Acid.

Initial compound		Yield	Boiling point (in °)	Pressure (in mm)	n _D ²⁰	d ₄ ²⁰	Phosphorus analysis	
Dialkyldithiophosphoric acid	Olefin						P calc'd (%)	P found (%)
1	2	3	4	5	6	7	8	9
(CH ₃ O) ₂ PS ₂ H	CH-COOC ₂ H ₅ CH-COOC ₂ H ₅	50	160-170	3.5	1.4960	1.2076	9.36	8.95 8.70
(C ₂ H ₅ O) ₂ PS ₂ H	CH-COOC ₂ H ₅ CH-COOC ₂ H ₅	59	157-162	3	1.4910	1.1742	8.65	8.62 8.50
(C ₃ H ₇ O) ₂ PS ₂ H	CH-COOC ₂ H ₅ CH-COOC ₂ H ₅	27	145	0.1	1.4880	1.1706	8.03	8.30 8.42
iso-(C ₃ H ₇ O) ₂ PS ₂ H	CH-COOC ₂ H ₅ CH-COOC ₂ H ₅	39	161	4	1.5440	1.0702	8.03	8.32 8.30
(C ₄ H ₉ O) ₂ PS ₂ H	CH-COOC ₂ H ₅ CH-COOC ₂ H ₅	40	125-128	0.025	1.4861	1.1078	7.5	7.72 7.92
iso-(C ₄ H ₉ O) ₂ PS ₂ H	CH-COOC ₂ H ₅ CH-COOC ₂ H ₅	15	117-130	0.04	1.4855	1.0642	7.5	7.94 7.84
(CH ₃ O) ₂ PS ₂ H	CH-COOCH ₃ CH-COOCH ₃	34.1	134.5	0.2	1.5070	1.2864	10.24	10.55 10.62

TABLE 5 --(continued)

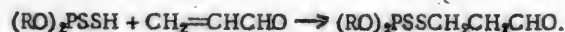
1	2	3	4	5	6	7	8	9
$(C_2H_5O)_2PS_2H$	$CH-COOCH_3$	50	116-120	0.025	1.4985	1.2237	9.38	9.47
	$CH-COOCH_3$							9.50
$(CH_3O)_2PS_2H$	$CH-COOC_3H_7\text{-iso}$	42.8	122.5-123	0.05	1.4810	1.1824	8.64	8.31
	$CH-COOC_3H_7\text{-iso}$							8.38
$(C_2H_5O)_2PS_2H$	$CH-COOC_3H_7\text{-iso}$	67.2	117-121	0.025	1.4815	1.1493	8.01	8.54
	$CH-COOC_3H_7\text{-iso}$							8.57
$(C_3H_7O)_2PS_2H$	$CH-COOC_3H_7\text{-iso}$	43.5	125-128	0.075	1.4785	1.1146	7.47	7.61
	$CH-COOC_4H_9\text{-iso}$							7.61
$(CH_3O)_2PS_2H$	$CH-COOC_3H_7\text{-iso}$	43.1	127.5-128	0.03	1.4835	1.1483	8.01	7.50
	$CH-COOC_4H_9\text{-iso}$							7.48
$(C_2H_5O)_2PS_2H$	$CH-COOC_4H_9\text{-iso}$	42.6	124-128	0.02	1.4775	1.1098	7.47	7.32
	$CH-COOC_4H_9\text{-iso}$							7.14
$(C_3H_7O)_2PS_2H$	$CH-COOC_4H_9\text{-iso}$	35.1	143-145	0.05 - 0.06	1.4822	1.0957	6.99	6.74
	$CH-COOC_4H_9\text{-iso}$							6.69

TABLE 6

Mixed Esters of Dithiophosphoric Acid Containing the Carboxyl Group

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(C_3H_7O)_2PS_2H$	$CH_2=CHCHO$	37	74	0.15	1.5040	1.1348	11.5	11.90
								11.28
$(C_2H_5O)_2PS_2H$	$CH_2=CHCHO$	34	80-81	0.05	1.5070	1.0984	12.85	12.90
								13.00
$(C_4H_9O)_2PS_2H$	$CH_2=CHCHO$	28	75-77	0.025	1.4955	1.0756	10.37	9.87
								9.88
$(CH_3O)_2PS_2H$	$(CH_3)_2C=CHCOCH_3$	70	93-96	0.05	1.5265	1.1979	12.08	12.41
								12.27

Dialkyldithiophosphoric acids add with comparative ease to aldehydes and ketones as well.



Compounds synthesized are given in Table 6.

EXPERIMENTAL

The synthesis of mixed dithiophosphoric acid esters was carried out in practically all cases under the following standard conditions: 1 mole of dialkyldithiophosphoric acid was gradually added, with good stirring, to 1 mole of olefin. The addition was carried out at such a rate that the temperature of the reaction mixture did not exceed 40-50°. After having added all of the dialkyldithiophosphoric acid, the reaction mixture was kept at room temperature until there was no further change in the free dialkyldithiophosphoric acid content, as determined by special titration tests with 0.1 N sodium hydroxide. Unreacted olefin was then distilled out of the reaction mixture, and the residue fractionated in vacuo.

The initial dialkyldithiophosphoric acid was synthesized by interaction of phosphorous pentasulfide with the corresponding alcohol [17].

SUMMARY

The reaction of dialkyldithiophosphoric acids with various unsaturated compounds has been studied. It has been demonstrated that satisfactory yields of mixed dithiophosphoric acid esters result on interaction of the compounds with dialkyldithiophosphoric acids.

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Received April 14, 1953

Scientific Institute for Fertilizers and
Insectofungicides

* VASKhNIL, = Lenin All-Union Academy of Agricultural Sciences.

** See Consultants Bureau Translation, page 2035.

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EFFECTS OF THE NATURE AND POSITION OF SUBSTITUENTS IN PHENYL RADICALS

(Ar')ArNHCOC(OH)Ar'₂ UPON 5-MEMBERED HETEROCYCLE CLOSURE. XIX.

P. A. Petyunin and V. S. Shklyaeu

One of us with I. S. Berdinsky [1] has demonstrated, in the case of ring closure for benzyl and p-tolyl acid arylamides, that the structure of the radicals on the carbinol carbon atoms exerts a profound effect upon the reaction rate. Following the period of elucidation of the mechanism of intramolecular condensations of hydroxy-carboxylic acid arylamides [2], it was then possible to clarify these facts and to design further in vestigational procedures. As is known, strain in ring formation and distance between reactive terminal groups [3,4] has an effect upon formation of cyclic systems. In forming rings of the same type, in our case of 5-membered rings, the indicated factors are of the same degree, and distinctions in ease of ring closure are thus caused by other factors.

For the present work compounds of the type ArNHCOC(OH)Ar'₂, where Ar = m-ClC₆H₄-, p-ClC₆H₄-, p-BrC₆H₄-, o-CH₃C₆H₄-, p-CH₃C₆H₄-, o-CH₃OC₆H₄-, m-CH₃OC₆H₄-, and p-CH₃OC₆H₄- were used as the starting materials.

The rate at which 5-membered heterocyclic closure took place in the indicated compounds was determined according to the following method: the optimum quantity of concentrated sulfuric acid was added along the wall of the test tube to 1 ml of the solution (0.015 mole of arylamide per liter of glacial acetic acid) at the given temperature. The reaction mass was kept at the same temperature for 1 minute on a water bath. Upon stirring, the coloration which appeared, depending upon the arylamide structure, disappeared after various time intervals. The appearance and disappearance times of color were determined by a second-meter, and were the rate indicator for ring closure (Table 1).

TABLE 1

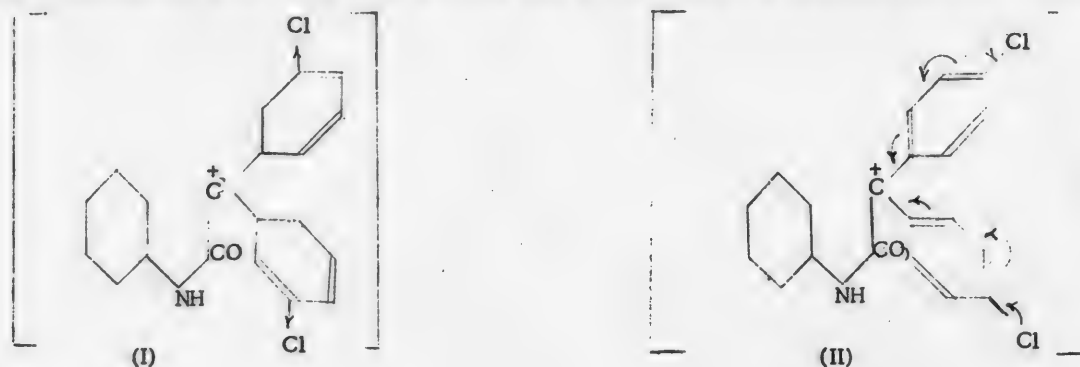
Closure Rate for 5-Membered Heterocycles with Arylamides of α -Hydroxycarboxylic Acids

No.	Formulas	Quantity of concentrated H ₂ SO ₄ (in ml)	Ring closure rate at 20°
1	C ₆ H ₅ NHCOC(OH)(C ₆ H ₄ Cl-m) ₂	7.5	Very high
2	C ₆ H ₄ NHCOC(OH)(C ₆ H ₄ Cl-p) ₂	4	12.5
3	C ₆ H ₅ NHCOC(OH)(C ₆ H ₄ Br-p) ₂	4	5
4	C ₆ H ₅ NHCOC(OH)(C ₆ H ₄ CH ₃ -p) ₂	1.5	12
5	o-CH ₃ OC ₆ H ₄ NHCOC(OH)(C ₆ H ₄ OCH ₃ -p) ₂	0.1	1
6	C ₆ H ₅ NHCOC(OH)(C ₆ H ₄ CH ₃ -o) ₂	2.5	1800

Note: Here and elsewhere the closure rate of the heterocycle is expressed in relative numbers. The rate of cyclic closure for arylamide No. 5 equal to 300 minutes, was taken as unity. Optimal quantities of sulfuric acid were used; they were determined for each arylamide, and represented the minimal amount for ensuring completeness of conversion of the arylamide into the heterocyclic compound. An increase in the quantity of sulfuric acid decreases markedly the rate of ring closure; a two-fold increase in the amount cuts down the condensation rate almost six-fold [2,5]. In the experiment involving the β -naphthalide of 4,4'-dimethoxybenzylic acid, a 75-fold increase in quantity of sulfuric acid decreased the ring closure rate almost 750-fold.

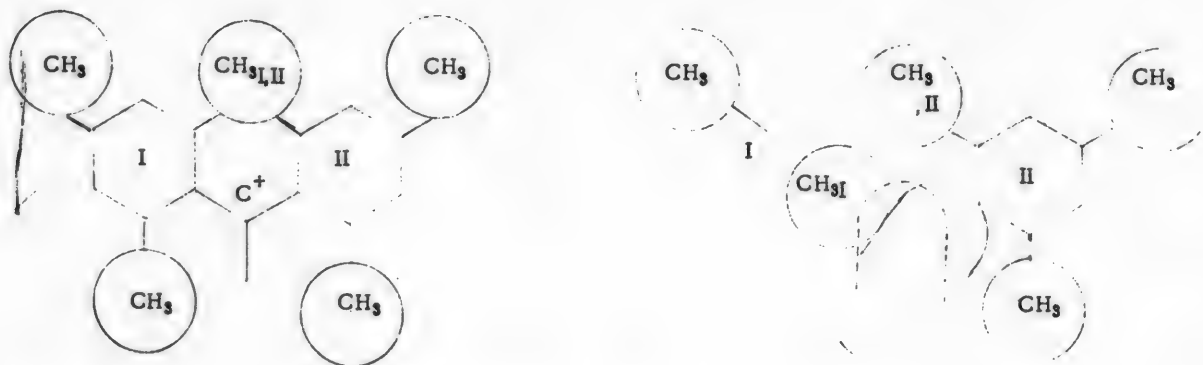
It can be seen from Table 1 that the closure rate for 5-membered heterocycles fluctuates from 1 to 1800; and more. The highest rate of closure takes place with arylamide No. 1. As a result of the electron-accepting

action of the chlorine atom, coupling of π -electrons of the benzene rings with carbonium carbon (I) decreases, and the degree of electrophilic attack of the latter increases, that is, is reflected in an extremely high reaction rate.



With arylamides Nos. 2 and 3 containing halogen in the p-position, the heterocycle closes at a slow rate. Under influence of the carbon atom positive charge the electron-donating properties of the halogens are intensified and the decrease in rate of cyclic closure can be explained by the presence of cation coupling with participation of the halogen atoms (II). The cyclization rate decreases upon introducing electron-donating substituents (arylamide No. 4) into the p-position; an even greater decrease takes place with arylamide No. 5. This is explained by the presence of cation coupling with participation of oxygen atoms of the methoxy group. With arylamide No. 6, the heterocycle closes 150-fold more rapidly than its p-isomer (arylamide No. 4). When substituents are introduced into the o-position, planarity of the cation is disrupted and coupling of the carbonium carbon with aryl radicals decreases [6], which therefore leads to considerable acceleration of ring formation.

It can be seen from the data given that ring closure rate is determined both by the nature of the substituent groups and by their position. It is of interest to compare the ease of ring closure for all possible isomers of arylamides with the same substituents on the phenyl radicals at the carbonyl carbon. With this object in mind, the rate of the heterocyclic closure for α -naphthylides of 2,2'-, 3,3'- and 4,4'-dimethoxybenzylidic acids was determined. It was found that the cyclic closure rate for the meta isomer at 20° with 0.5 ml of H_2SO_4 was equal to 1200, and for the ortho-isomer with 1.5 ml, equal to 37.5, and for the para isomer with 0.1 ml, equal to 5.



Thus, from the point of view of substituent positions, the cyclic closure rate decreases in the order $m > o > p$.

With respect to the theoretical relationship, it was important to study the possibility of intramolecular ring closure for those arylamides in which all four ortho-positions of the phenyl radicals at the carbinol carbon are occupied by substituents. For this purpose the α -aniside of dimesitylglycolic acid was synthesized. An attempt to close the ring failed. Steric hindrance is strongly exhibited for the cation of the halochromic salt of this arylamide, barring the possibility of a planar arrangement of the mesityl radicals (Fig. 1). Because of

this, radicals are arranged in interperpendicular planes. Here the CH_3 group (Fig. 2) coming in contact with the benzene ring bound with nitrogen (drawn as a broken line) mitigates against a position favorable for closure of a 5-membered planar ring.

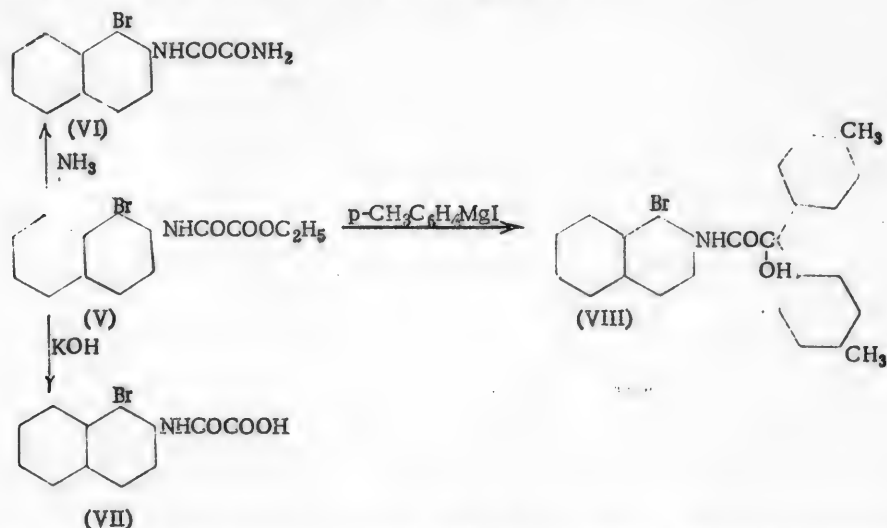
It has been further established that with α and β -naphthalides of 4,4'-dimethoxybenzylic acid, cyclic closure proceeds at varied speed (Table 2).

TABLE 2
Closure Rates of 5-Membered Heterocycles for α - and β -Naphthalides
of 4,4'-Dimethoxybenzylic Acid.

Formula	Quantity of conc. H_2SO_4 (in ml)	Ring closure rate at 20°
$\beta\text{-C}_{10}\text{H}_7\text{NHCOC(OH)(C}_6\text{H}_4\text{OCH}_3)_2$ (III)	0.1	1.25
$\alpha\text{-C}_{10}\text{H}_7\text{NHCOC(OH)(C}_6\text{H}_4\text{OCH}_3)_2$ (IV)	0.1	5

Upon condensation (III), the central carbon atom becomes coordinated with the α -position of the naphthyl radical, and with condensation (IV) — the β -position. But if the α -position is more nucleophilic than the β -, the rate of condensation (III) then should be greater than (IV). However, (IV) condenses four times more rapidly than (III),

explainable by a lesser steric accessibility of the α -position upon coordination with a central carbon atom containing two phenyl radicals. Similar cases are known [7] in naphthalene reactions. One of us [8] has shown that the 1-bromo-2-naphthalide of benzylic acid forms a β, β -condensation product. In connection with the fact it was of interest to compare cyclic closure rates for α, β - and β, β -condensations. For this purpose, synthesis of the 1-bromo-2-naphthalide of p-tolylic acid was carried out according to the scheme:



The amide (VI) resulted by the action of ammonia upon the ethyl ester of 1-bromo-2-naphthyl oxamic acid (V), and upon hydrolysis, 1-bromo-2-naphthyl oxamic acid (VII) resulted. The 1-bromo-2-naphthalide of p-tolylic acid (VIII) was synthesized by interacting (V) with p-tolylmagnesium iodide. It was found that the cyclic closure rate for (VIII) at 20°, with 1.5 ml of H_2SO_4 , was equal to 12, and for the β -naphthalide of p-tolylic acid (IX) under the same conditions — 11.5. Thus, condensation (VIII) and (IX) rates are almost the same despite the fact that steric hindrances occur with α, β -condensation (IX). The decreased rate of 5-membered ring closure for β, β -condensation (VIII) is explained by a weakening of the nucleophilic reaction center due to manifestation of an electron-accepting action on the part of bromine. The effect of a nucleophilic reaction center upon the condensation of the m-aniside of p-tolylic acid has been described [1].

EXPERIMENTAL

The anilide of 3,3'-dichlorobenzylic acid. 7.7 g (0.04 mole) of oxanilic acid ethyl ester was added to m-chlorophenylmagnesium iodide obtained from 42.5 g (0.18 mole) of m-chloriodobenzene and 4.4 g (0.18 mole) of magnesium in 100 ml of ether. The reaction mass was decomposed with 5% hydrochloric acid. The ether layer was separated, and to remove the solvent as well as volatile reaction products, was distilled with steam. An oily liquid was left in the distilling flask, which crystallized rapidly on standing. Long, colorless needles (from toluene), with m.p. 170-171°. Insoluble in water and gasoline; soluble, upon heating, in alcohol, benzene, acetone, toluene, acetic acid, and ether. Formed an evanescent reddish-violet coloration with concentrated sulfuric acid. 7.3 g of the substance was obtained (49% calculating on the basis of the ethyl ester of oxanilic

acid taken for reaction).

0.2506 g substance: 14.3 ml 0.05 N H_2SO_4 . 0.2957 g substance: 15.9 ml 0.05 N H_2SO_4 . Found %: N 3.99, 3.76. $\text{C}_{20}\text{H}_{15}\text{O}_2\text{NCl}_2$. Calculated %: N 3.76.

The anilide of 4,4'-dichlorobenzylidic acid. Initial substances: 23.6 g (0.1 mole) of p-chloriodobenzene* 4.3 g (0.0022 mole) of oxanilic acid ethyl ester and 2.3 g (0.1 mole) of magnesium.

After decomposition of the reaction mixture, the crystalline mass was isolated from the ether layer. Upon crystallization from benzene—colorless platelets, m.p. 181.5–182.5°. Yield 4.6 g (55 % of theory). Soluble, upon heating, in alcohol, benzene, acetic acid, acetone and ether; insoluble in water and gasoline. Reddish-violet coloration with concentrated sulfuric acid, disappearing upon standing or heating.

Found %: N 3.74, 3.94. $\text{C}_{20}\text{H}_{15}\text{O}_2\text{NCl}_2$. Calculated %: N 3.76.

The anilide of 4,4'-dibromobenzylidic acid. Taken for reaction were: 6.6 g (0.034 mole) of oxanilic acid ethyl ester, 34.4 g (0.15 mole) of p-dibromobenzene and 3.6 g of magnesium. Thin needles (from benzene) with m.p. 192–194°. Insoluble in water and gasoline; soluble in alcohol, ether, benzene and toluene. Violet coloration with concentrated sulfuric acid, fading on standing. Yield was 5.1 g (32.5 % of theory).

Found %: N 2.66, 2.76. $\text{C}_{20}\text{H}_{15}\text{O}_2\text{NBr}_2$. Calculated %: N 3.04.

α -Naphthalide of 3,3'-dimethoxybenzylidic acid.** Taken for reaction were: 6 g (0.025 mole) of α -naphthyloxamic acid ethyl ester, 29 g (0.13 mole) of m-iodoanisole, 3 g (0.13 mole) of magnesium. The product crystallized as colorless platelets from alcohol, m.p. 151–152.5°. Insoluble in water, gasoline and ether; readily-soluble in alcohol, acetic acid and benzene. Momentary brown coloration with concentrated sulfuric acid. 4.8 g (46.8 % of theory) was obtained.

Found %: N 3.66, 3.5. $\text{C}_{25}\text{H}_{23}\text{O}_4\text{N}$. Calculated %: N 3.37.

The o-anisidide of dimesitylglycolic acid. An ether solution of 5.9 g (0.027 mole) of 2-methoxyoxanilic acid ethyl ester was gradually added to mesitylmagnesium bromide prepared from 24 g (0.12 mole) of bromomesitylene and 2.9 g (0.125 mole) of magnesium in 80 ml of ether. The reaction mass was heated on a water bath 4 hours. The reaction products crystallized slowly to colorless platelets, m.p. 162–164° from gasoline. An orange-red coloration formed with concentrated sulfuric acid which did not disappear, even upon heating. Yield was 2.5 g (22 % of theory).

Found %: C 77.65, 77.18; H 7.65, 7.47; N 3.05, 2.95. Active H 2.2, 2.15. $\text{C}_{27}\text{H}_{31}\text{O}_5\text{N}$. Calculated %: C 77.70; H 7.44; N 3.35. Active H 2.

Attempt to close the ring in the o-anisidine of dimesitylglycolic acid. 10 ml of concentrated sulfuric acid was added to an acetate solution of 0.5 g of the o-anisidide of dimesitylglycolic acid. The orange-yellow coloration did not fade, even after 3 hours of heating on a boiling water bath. The product was isolated by the usual procedure. Colorless platelets (from gasoline), m.p. 162–164°. 0.4 g, or 80 % of the product taken for reaction, was obtained. Identity of this substance with the o-anisidide of dimesitylglycolic acid was proved by the mixed melting test.

The amide of 1-bromo-2-naphthyloxamic acid. Ammonia was passed into a solution of 2 g of 1-bromo-2-naphthyloxamic acid ethyl ester in 10 ml of alcohol, with cooling. The resulting white precipitate was filtered off and dried in air. Upon crystallizing from benzene—colorless needles with m.p. 231–232°. 1.75 g was obtained (96.1 % of theory). Poorly-soluble in alcohol, ether and gasoline; soluble with heating in benzene and toluene.

Found %: N 9.66, 9.70. $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}_2\text{Br}$. Calculated: N 9.55.

1-Bromo-2-naphthyloxamic acid. 2 g of 1-bromo-2-naphthyloxamic acid ethyl ester was heated with 250 ml of 0.5 % sodium hydroxide. The hot, transparent solution was acidified with concentrated hydrochloric acid and the resulting precipitate treated by the usual procedures. Fine needles (from benzene), with m.p. 158–159° (with decomposition). 1.8 g was obtained (99 % of theory). Readily-soluble in alcohol; soluble in benzene upon heating, difficultly-soluble in gasoline, ether and water.

* According to the author's data, p-chloriodobenzene reacts with the iodine atom, which is in agreement with the data of Michalescu and Garagea [9] and which refutes the data of Runge [10].

** This substance, as well as its condensation product, 3,3-bis(3-methoxyphenyl)-6,7-benzohydroxyindole, has been synthesized by I. V. Sannikova and N. N. Staroverova.

Found %: N 4.64, 4.61. $C_{18}H_{13}O_3NBr$. Calculated %: N 4.77.

1-Bromo-2-naphthalide of 4,4'-dimethylbenzylidic acid. Reaction was effected between 6.44 g (0.02 mole) of 1-bromo-2-naphthyloxamic acid ethyl ester and 0.09 mole of p-tolyl magnesium iodide. Crystallized from benzene as colorless needles with m.p. 158-160°. Readily-soluble in ether, toluene and acetic acid, somewhat less so in alcohol, poorly so in gasoline. With concentrated sulfuric acid, slowly gave a fading raspberry-red coloration. The yield was 3.5 g (38% of theory).

Found %: N 2.79, 3.09. $C_{26}H_{22}O_3NBr$. Calculated %: N 3.04.

3,3-Bis-(3-chlorophenyl)-hydroxyindole. 3 g of 3,3'-dichlorobenzylidic acid anilide was dissolved in 15 ml of concentrated sulfuric acid. After decoloration, the reaction mass was poured into water. Thin needles (from glacial acetic acid) with m.p. 248-250°. Soluble in alcohol, benzene, toluene and acetic acid; insoluble in water and gasoline. Yield was 2 g (70% of theory).

Found %: N 3.68, 3.65. M 332, 333 (camphor). $C_{20}H_{15}ONCl_2$. Calculated %: N 3.96. M 354.

3,3-Bis-(4-chlorophenyl)-hydroxyindole. There was taken for reaction 1 g of 4,4'-dichlorobenzylidic acid anilide in 10 ml of concentrated sulfuric acid. Upon crystallization from 70% alcohol - needles grouped in clusters, with m.p. 186-187°. Readily-soluble in alcohol, ether, benzene, chloroform and toluene; insoluble in water and gasoline. Yield was 0.5 g (52.3% of theory).

Found %: N 3.74, 3.94; Cl 20.4. M 355.1, 330.8 (in camphor). $C_{20}H_{15}ONCl_2$. Calculated %: N 3.96; Cl 20.6. M 354.

3,3-Bis-(4-bromophenyl)-hydroxyindole. 3 g of 4,4'-dibromobenzylidic acid anilide in 25 ml of glacial acetic acid was condensed with concentrated sulfuric acid. A fine crystalline powder (from dilute alcohol) with m.p. 198-200°. Readily-soluble in alcohol and glacial acetic acid, poorly so in benzene, toluene and gasoline. 0.9 g was obtained (31% of theory).

Found %: N 3.38, 3.06. M 432, 435.7 (in camphor). $C_{22}H_{15}ONBr_2$. Calculated %: N 3.16. M 443.

3,3-Bis-(4-tolyl)-7-bromo-5,6-benzhydroxyindole. Initial substances: 2 g of the 1-bromo-2-naphthalide of 4,4'-dimethylbenzylidic acid in 15 ml of glacial acetic acid and 10 ml of concentrated sulfuric acid. Soluble, upon heating, in alcohol and gasoline, in the cold - in benzene and glacial acetic acid. Crystallized from glacial acetic acid as colorless platelets, m.p. 263° at 23mm. Yield was 0.6 g (31% of theory).

Found %: Br 17.95, 17.96. $C_{25}H_{20}ONBr$. Calculated %: Br 18.08.

3,3-Bis-(3-methoxyphenyl)-6,7-benzhydroxyindole. 30 ml of concentrated sulfuric acid was added to a solution of 3 g of the 3,3-dimethoxybenzylidic acid of α -naphthalide in glacial acetic acid. Insoluble in water, poorly so in alcohol; soluble in acetic acid and toluene with heating. Colorless, fine needles (from acetic acid) with m.p. 200.5-203°. 1.8 g was obtained (62.7% of theory).

Found %: N 3.78, 3.62. $C_{26}H_{22}O_3N$. Calculated %: N 3.54.

SUMMARY

1. In accordance with the mechanism of intramolecular condensation of hydroxycarboxylic acid arylamides, a method, based upon the ability of halochromic salts of arylamides to lose their coloration as the result of intramolecular ring closure, has been used to determine 5-membered heterocyclic closure.

2. It has been established that the rate of 5-membered ring closure for compounds of the $ArNHCO(OH)Ar_2$ type is determined both by the nature of the substituting groups and by their position in Ar' . Electron-accepting constituents intensify the electrophilic nature of the carbonium carbon of the halochromic cation of an arylamide and accelerate ring closure; groups with converse action decrease the electrophilic nature of the carbonium carbon and decrease the reaction rate. From the point of view of substituent position, the rate of ring closure takes the order: $m > o > p$.

3. The effect of steric hindrance upon ring closure has been studied, using as the example o-tolyl and dimethylglycolic acid anilides. It has also been determined in this study that arylamides in which all four ortho positions of the phenyl radicals attached to the carbinol carbon fail to undergo condensation reaction because of steric hindrance.

4. The rate of 5-membered ring closure has been studied for the α - and β -naphthalides of 4,4'-dimethoxybenzylic acid and also for α,β - and β,β -condensations. It has been determined in this case that the ring closes 4 times more rapidly for the α -naphthalide of 4,4'-dimethoxybenzylic acid than for the β -isomer. With α,β - and β,β condensations, the ring closes at practically the same speed. An explanation for these facts has been given.

5. A number of arylamides of α -hydroxycarboxylic acids, derivatives of 3,3-diarylhydroxyindole, and other compounds not described in the literature, have been synthesized and their properties studied.

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Received November 3, 1952

Molotov Pharmaceutical Institute

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RESEARCH IN THE FIELD OF QUINONES

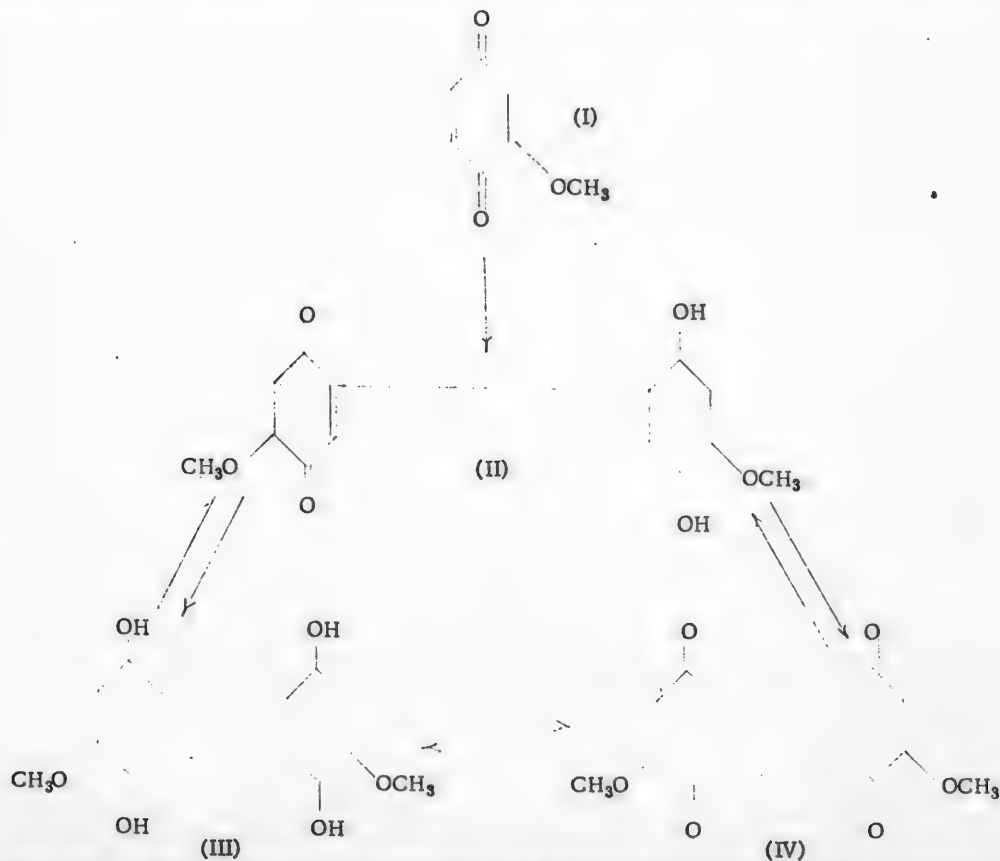
IV. METHOXYQUINONE CONVERSION UNDER THE INFLUENCE OF ACIDS

I. S. Ioffe and A. F. Sukhina

A method is widely used for synthesizing various chloroquinones, consisting in the treatment of quinone with hydrochloric acid, followed by subsequent oxidation of the resulting addition product, which, in one of its tautomeric forms, represents the corresponding chlorohydroquinone. Thus, for example, the chloroquinone is synthesized according to such method, starting with *p*-benzoquinone. However, this method is unsuitable for the synthesis of chloromethoxyquinones [1], since the methoxyquinone, in the presence of acids, among them hydrochloric, forms a condensation product of two molecules, which separates in the form of violet-blue needle crystals.

Experiments by the authors have demonstrated that this blue substance can be obtained in quantitative yield very smoothly from the methoxyquinone by addition of hydrochloric or sulfuric acid to a dilute aqueous acetate solution of the methoxyquinone.

Erdtman [2] assumed that the blue substance forms as a result of the condensation of two molecules of methoxyquinone (I) or of methoxyquinone and methoxyhydroquinone, with the appearance of a diphenyl bond in the *p*-position to the methoxyl groups, and represents the intramolecular quinhydrone (II). Indeed, upon reduction of the blue substance, a leuco compound was obtained, from which, after demethylation, there resulted the already described 2,4,5,2',4',5'-hexahydroxydiphenyl. Hence it follows that the indicated leuco compound represents 2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl (III), and that the intramolecular quinhydrone resulting from it by moderate oxidation has the structure (II). However, upon treating the leuco compound (III), or the blue substance (II) with strong oxidants, for example with chromic acid, there results yellow dimethoxydiquinone (IV).

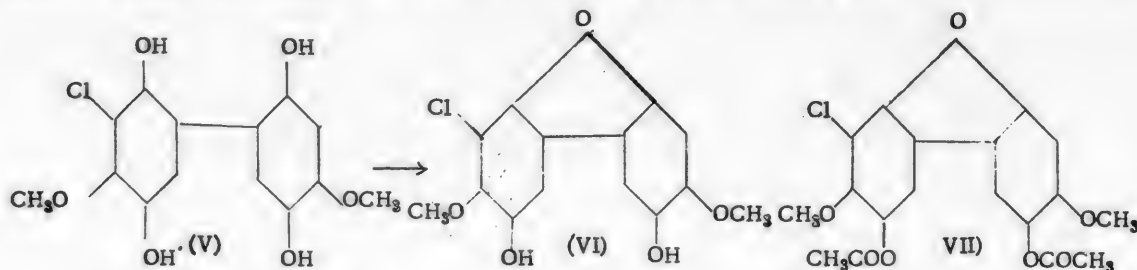


Acid condensation of methoxyquinone is specific for this compound and is conditioned by the effect of the methoxy group. Under analogous conditions such a reaction does not go with either non-substituted p-benzoquinone or its derivatives which contain other substituents.

The possibility came to mind that this reaction ability of methoxyquinone might be used for deriving various unsymmetrical derivatives of diphenyl, through the condensation of methoxyquinone with phenols. However, experiments have not confirmed this assumption. Upon adding hydrochloric acid to a dilute acetate solution of methoxyquinone with phenol, guaicol or hydroquinone, in equimolecular mixture, a pure precipitate of the blue intramolecular quinhydrone (II) resulted in all cases, in amounts corresponding to the weighed methoxyquinone portions used in the reaction. This condensation proceeded only slightly more rapidly in the presence of hydroquinone. It follows from the given experiments that the condensation in question is specific for methoxyquinone, and is conditioned by the combined effect of the methoxyl group and quinoid group.

The author's investigation has demonstrated, however, that the interaction of methoxyquinone with hydrochloric acid is not limited to formation of the blue substance (II). Along with it, some colorless substance is also formed, which, in distinction to compound (II), dissolves in acetic acid and alcohol, separating from these solvents, upon crystallization, as fine, white, needle crystals, melting sharply at 230-231°. This new substance contained chlorine. The author observed that the quantity of colorless chlorine-containing compounds increased both with increased treatment time of the methoxyquinone with hydrochloric acid, and with increased hydrochloric acid concentration; at the same time, the quantity of blue substance (II) decreased accordingly. Under the determined conditions the chloroderivative resulted as the principal reaction product. It follows from these observations that this colorless substance forms not as a result of direct interaction of hydrochloric acid with methoxyquinone, but rather represents an interaction product between hydrochloric acid and the intermediate-forming blue compound (II). In fact, upon shaking a suspension of the earlier prepared and crystallized compound (II) with concentrated sulfuric acid, the blue crystalline precipitate gradually transformed into colorless crystals, which, after purification, melted at 230-231°. Such transformation proceeds much more rapidly and quantitatively upon adding concentrated hydrochloric acid to a boiling suspension of the blue compound (II) in acetic acid.

It was most logical to assume that the chloroderivative obtained by the authors forms as the result of hydrogen chloride addition to intramolecular quinhydrone (I) at the expense of its quinoid radical, and that it represents 3-chloro-2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl (V). However, quantitative acetylation in pyridine solution has shown that two and not four hydroxy groups are present. In the tetrahydroxydiphenyl derivative (V), it is indeed possible to close the furane ring at the expense of two hydroxy groups in the o-position to the diphenyl bond, with formation of the hydroxydiphenyl derivative (VI) containing only two hydroxy groups.



It was necessary to ascertain the structure of the chloroderivative obtained by the authors which melted at 230-231°. As analytical determinations have indicated, the acetyl derivative obtained from it possessed a cyclic oxide structure (VII).

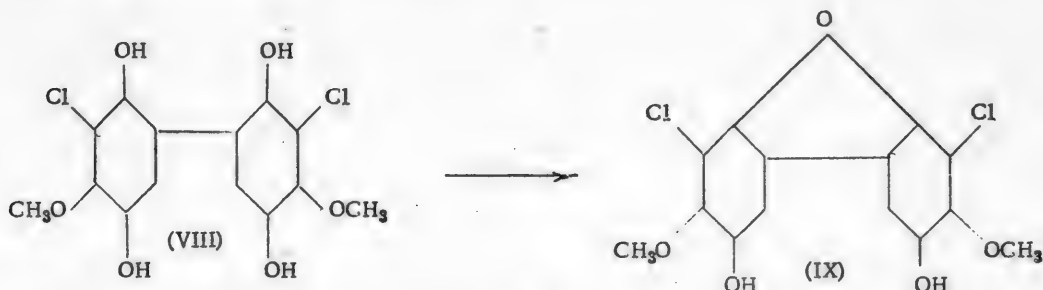
However, a cyclic oxide structure for the acetyl derivative does not suffice as complete proof of identity of structure of the non-acetylated substance, since furane ring closure could occur during the acetylating process. The possibility of such an occurrence was rejected by the authors on the basis of the following experiments. The authors carried out acetylation of 2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl (II), in pyridine solution. Thereupon, the acetylation of all four hydroxy groups proceeded quantitatively, with formation of the tetraacetyl derivative.

This experiment demonstrated that tetrahydroxyderivatives of the diphenyl type (II), and to this also belongs the substance of structure (V), do not convert to the diphenyloxide derivatives with water evolution, upon treatment with acetic anhydride in pyridine solution, but instead form tetraacetyl derivatives.

It follows from what has been stated above that the colorless chloro-derivative obtained by interaction of the blue quinhydrone (II) with hydrochloric acid contains the oxide ring and has the structure (VI) even before the acetylation. Direct and final proof of this fact was given by determination of active hydrogen (according to Tserévitinov-Chugaev), which indicated the presence of only two hydroxyl groups in the given compound. Confirmation of such a structure can be seen from the fact that the given substance also gave a stable alkaline solution, from which, upon acidification, the substance was isolated in unchanged form. At the same time, all compounds of the type (III) structure, i.e. containing two hydroquinone groupings, oxidize very readily.

Thus, the authors' investigation has indicated that upon interaction of the blue quinhydrone (II) with hydrochloric acid, along with hydrogen chloride addition to the quinoid ring, there also proceeds closure of the oxide ring of the intermediate diphenyl derivative [V] under the effect of hydrochloric acid, with formation of the 3-chloro-5,5'-dihydroxy-4,4'-dimethoxyoxide of diphenyl (VI) as the final product.

During the progress of these works, the authors decided to study also interaction of the corresponding diquinone (VI) with hydrochloric acid. The authors surmised that two hydrogen chloride molecules could be added to this compound containing two quinoid groupings, and that oxide ring closure would be possible for the intermediate diphenyl derivative (VIII) formed, with resulting conversion to the 3,3'-dichloro-5,5'-dihydroxy-4,4'-dimethoxyoxide of diphenyl (IX).



The experiments confirmed our assumptions. Upon addition of concentrated hydrochloric acid to a boiling solution of dimethoxydiquinone (IV) in acetic acid, a colorless precipitate resulted from the solution, which, after crystallization, melted at 235-236°. The acetyl derivative crystallized in the form of colorless needles, melting at 252-253°. Determination of chlorine, methoxyl and hydroxyl groups confirmed that the substance obtained from dimethoxydiquinone has only two hydroxy groups and is of the structure (IX).

Erdtman [2] has also studied the interaction of dimethoxyquinone with hydrochloric acid. However, he limited himself to passage of hydrogen chloride through a solution of dimethoxydiquinone in chloroform, and obtained an addition product of two hydrogen chloride molecules to the dimethoxydiquinone molecule. Erdtman did not isolate this product in the pure state, since it proved to be so unstable that attempts to crystallize it resulted in decomposition to the original materials. This product also decomposed upon heating with acetic anhydride. However, during this operation, there was, nonetheless, a small yield of new substance melting at 253°, to which Erdtman hypothetically attributed the structure (IX). On the basis of the authors' investigations, such a structure can be accepted as accurate, and the formation of such a product can be understood, since upon heating with acetic anhydride in the presence of hydrogen chloride (resulting from decomposition of larger amounts of addition products), there should take place both formation of the diphenyl derivative (VIII) and closure of the furane ring, with conversion to derivatives of diphenyl oxide (IX); the latter acetylates to form the diacetyl derivative. The diphenyl oxide derivative (IX) results in almost quantitative yield upon shaking dimethoxydiquinone (IV) in acetate suspension with concentrated hydrochloric acid. The precipitate was at first yellow, acquiring a green shade, and then through blue to colorless. In distinction to the addition product described by Erdtman, the resulting substance did not decompose upon heating, and crystallized from 80% acetic acid to form colorless needles with m.p. 235-236°.

This investigation in which the main purpose was a study of methoxyquinone transformations in the presence of hydrochloric acid, was also of interest to the authors for another reason, namely that the authors were able to carry out specific comparisons of these conversions with acid conversions observed by the authors for methoxyfuchsones. Under effect of the latter, fuchsones derivatives containing methoxyl groups converted, in the presence of hydrochloric acid into the corresponding fluorene derivatives; here the aromatic radicals added in the p-positions to the methoxyl groups. Thus, the fluorene derivatives resulted from dimethoxybenzaurine [3].

For a large number of quinones, the methoxyl groups impart to such compounds containing them distinctive properties. In particular there is the ability of methoxyquinone to form, in the presence of acids, condensation products of two molecules with a compound containing aromatic nuclei in the p-positions to the methoxyl groups. A comparison of this reaction with the above-described reaction of methoxyfuchsonic acid conversions has indicated that both reactions are relative and are conditioned by the peculiar effect of methoxyl groups.

EXPERIMENTAL

Synthesis of condensation products with a diphenyl structure from methoxyquinone. Intramolecular quinhydrone (II). 10 g of methoxyquinone (I) was dissolved with heating in 100 ml of glacial acetic acid and the resulting solution poured into 2 liters of 1% hydrochloric acid. A blue precipitate gradually began to form from the solution. After standing for 48 hours, the resulting precipitate was filtered off, washed with water and dried. The yield was 9.5 g or 95% of theory. The resulting precipitate melted at 230° and after recrystallization from pyridine, melted at 238°. This compound was almost insoluble in water and alcohol, and very poorly soluble in acetic acid.

2,5,2',5'-Tetrahydroxy-4,4'-dimethoxydiphenyl (III). 3 g of the blue intramolecular quinhydrone was introduced into 10 ml of acetic acid, and to the suspension was added 3 g of zinc dust, and the mixture heated to complete dissolution of the blue precipitate, and decoloration of the solution. The latter was filtered and the filtrate added to 50 ml of water containing several drops of sodium bisulfate. The resulting precipitate was filtered and crystallized from dilute alcohol. The substance obtained was in the form of colorless crystals melting at 210° with decomposition. The yield was 1.8 g, or 60% of theory.

Upon heating with pyridine mixed with acetic anhydride, the tetracetyl derivative (VIII) was obtained, which, after crystallization from alcohol, melted at 186-187°.

Qualitative acetylation gave the following results: 0.1486 g substance: 21.7 ml 0.1 N NaOH. Found % OH 24.82. $C_{18}H_{16}O_8(OH)_4$. Calculated % OH 24.45.

Dimethoxydiquinone (IV). 3 g of the blue intramolecular quinhydrone was ground finely in a mortar, and then 300 ml of water was introduced, containing 3 g of chromic acid. The resulting suspension was shaken to the point that the blue residue was completely converted to a canary-yellow. The resulting precipitate was filtered off, washed with water and dried. The yield was quantitative. The reaction product melted at 205-207°. After crystallization from acetic acid, it resulted in yellow needles with an m.p. of 212-214°.

5,5'-Dihydroxy-4,4'-dimethoxy-3-chlorooxide of diphenyl (VI). 1) One gram of methoxyquinone was dissolved in 10 ml of acetic acid and to the resulting solution 20 ml of concentrated hydrochloric acid was added. A colorless product precipitated out slowly in crystalline form. After holding for 48 hours, the resulting mixture was poured into 100 ml of water, the precipitate formed filtered off, washed with water and dried. The yield was 0.8 g, or 75% of theory.

2) 3 g of the blue substance was suspended in 30 ml of acetic acid, to the suspension added 10 ml of concentrated hydrochloric acid, and the mixture heated with stirring on a boiling water bath. At 60-70° the precipitate was already decolorized, acquiring a light-gray color. The suspension so formed was poured into 150 ml of hot water and after cooling the precipitate was filtered off, washed and dried. The yield was 3 g, or 95% of theory.

The substance obtained in this manner melted at 215-220°. After crystallization from acetic acid, colorless needles resulted, with m.p. 230-231°.

The substance was poorly soluble in water, moderately so in alcohol and glacial acetic acid; soluble in aqueous alkali, forming a stable solution, upon acidification of which there separated out the unchanged product. Melted at 230-231°. It formed the acetyl derivative upon heating with pyridine and acetic anhydride mixture, which, after crystallization from acetic acid, melted at 220-221°.

The non-acetylated substance.

0.2916, 0.2450 g substance: 20.2, 16.5 ml 0.1 N NaOH. 0.1022, 0.1075 g substance: 16.2, 15.6 ml CH_4 . 0.1002 g substance: 0.1548 g AgI. Found % OH 11.77, 11.45, 12.1, 11.1; OCH_3 20.39. $C_{18}H_{14}O_5Cl$. Calculated % OH 11.55; OCH_3 21.05.

The acetyl derivative.

0.1271, 0.1230 g substance: 0.1588, 0.1557 g AgI. Found % OCH_3 16.52, 16.73. $C_{18}H_{16}O_7Cl$. Calculated % OCH_3 16.4

5,5'-Dihydroxy-4,4'-dimethoxy-3,3'-dichlorooxide of diphenyl (IX). 5 g of dimethoxydiquinone was introduced into 25 ml of glacial acetic acid, and to the boiling suspension 25 ml of concentrated hydrochloric acid was added, after which all of the mixture was brought to boiling. Thereupon a light-gray reaction product separated. 100 ml of hot water was added and after cooling was filtered, washed with water and dried. The yield was 4.8 g, or 85% of theory. The crude product melted at 220-225°. After crystallization from acetic acid—colorless needles with m.p. 235-236°.

The substance was poorly soluble in water. It crystallized from alcohol and acetic acid. It was soluble in alkali. Upon acidification of the alkaline solution, it separated in unaltered form. Melting point 235-236°. It formed the acetyl derivative upon heating with pyridine and acetic anhydride mixture, which, after recrystallization from acetic acid resulted as colorless needles, m.p. 252-253°.

Non-acetylated substance.

0.2238, 0.2422 g substance: 13.7, 15.1 ml 0.1 N NaOH. 0.1040, 0.1243 g substance: 13.8, 17.0 ml CH_4 . 0.1194, 0.1510 g substance: 0.1054, 0.1296 g AgCl. Found % OH 10.45, 10.52, 10.1, 10.5; Cl 21.44, 21.25. $\text{C}_{16}\text{H}_{10}\text{O}_5\text{Cl}_2$. Calculated % OH 10.37; Cl 21.6.

The acetyl derivative.

0.1012 g substance; 0.1155 g AgI. Found % OCH_3 15.01. $\text{C}_{18}\text{H}_{14}\text{O}_7\text{Cl}_2$. Calculated % OCH_3 15.08.

SUMMARY

The methoxyquinone, in contrast to other quinones, forms a condensation product of two molecules under the influence of mineral acids, with appearance of the diphenyl bond in the p-position to the methoxyl groups. This compound is blue in color, and is found to be the intramolecular quinhydrone, which, upon reduction, converts to colorless 2,5,2',5'-tetrahydroxy-4,4'-dimethoxy diphenyl, and upon oxidation, to the yellow dimethoxydiquinone.

Upon interacting methoxyquinone with concentrated hydrochloric acid, the reaction is not limited to formation of the blue intramolecular quinhydrone. To the latter a molecule of hydrogen chloride is added at the expense of the quinoid group, and with 3-chloro-2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl, the furane ring is closed under the influence of hydrochloric acid, with water evolution and formation of the corresponding colorless diphenyl oxide derivative, m.p. 230-231° (diacetyl derivative, m.p. 220-221°).

In an analogous fashion, upon treating dimethoxydiquinone with hydrochloric acid, two hydrogen chloride molecules add to the former, with intermediate formation of 3,3'-dichloro-2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl, under which reaction conditions closure of the furane ring occurs, with conversion to the corresponding dichloroderivative of diphenyloxide with m.p. 235-236° (diacetyl derivative, m.p. 252-253°).

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Received March 19, 1953.

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THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN CARBON TETRACHLORIDE-METHYL ALCOHOL MIXTURE

G. A. Razuvaev, B. N. Moryganov and V. A. Stepushkina

Carbon tetrachloride, previously considered an almost inactive compound, has been found capable of adding to olefins in the presence of peroxides and light [1]. It has been considered usually that the action of ultraviolet light and benzoyl peroxide or acetyl peroxide produces analogous reactions. However, A. E. Borisov has been able to demonstrate that carbon tetrachloride and diphenylmercury reactions take a different course of action under the influence of acetyl peroxide as compared with the same reaction proceeding under the influence of ultraviolet light. In the first case benzotrichloride is formed, i.e., interaction of the phenyl radical with the CCl_3 radical occurs, and in the second case just dimerization, leading to hexachloroethane.

The authors have indicated a different direction for the reaction of carbon tetrachloride with alcohols under the influence of temperature and ultraviolet light [3]. Upon heating carbon tetrachloride with methyl alcohol to 200-210°, there proceeds formation of chloroform, formaldehyde and HCl , but under the influence of ultraviolet light CCl_3 radicals give hexachloroethane.

It was of interest to clarify whether or not benzoyl peroxide will initiate reaction of carbon tetrachloride with alcohols, and if this reaction goes, whether it will follow the direction of thermal reaction or photoreaction. With thermal decomposition of benzoyl peroxide in carbon tetrachloride and methyl alcohol mixture, the following can be hypothesized.

1. Benzoyl peroxide will react only with carbon tetrachloride:



2. Benzoyl peroxide will react only with methyl alcohol.

3. Benzoyl peroxide will initiate reaction between carbon tetrachloride and methyl alcohol, as indicated above [3].

It has been found that benzoyl peroxide reaction with alcohols is almost non-existent in the literature: the decomposition kinetics of benzoyl peroxide in alcohol without the evolution of reaction product [4] has been studied, and only the reaction of benzoyl peroxide with isobutyl alcohol has been studied in some detail [5].

The authors therefore, set up experiments on the decomposition of benzoyl peroxide in methyl alcohol over a wide temperature range (from 70 to 150°), and have determined that reaction proceeds with formation chiefly of benzoic acid, methylbenzoate and formaldehyde [2]. Reaction (3) to give benzene and CO_2 proceeded, but to a lesser degree.



In carrying out experiments on initiation of the carbon tetrachloride and methyl alcohol reaction by benzoyl peroxide, there resulted chloroform hexachloroethane, formaldehyde, HCl , benzoic acid, methylbenzoate, phthalic acid and CO_2 .

The formation of hexachloroethane and phthalic acid attested to the fact that benzoyl peroxide reacts with carbon tetrachloride.

Isolation of benzoic acid, methyl benzoate and formaldehyde indicated that the benzoyl peroxide reacted with methyl alcohol.

It may be said, however, that benzoyl peroxide initiated the reaction between carbon tetrachloride and methyl alcohol, which is indicated by evolution of HCl and separation of chloroform. It can be seen definitely, therefore, that the reaction, to some degree, proceeds according to equation (4):



EXPERIMENTAL

I. Thermal decomposition of benzoyl peroxide in methyl alcohol. Heating of the components was carried out both in a flask with condenser, and in sealed tubes at higher temperatures. *

a) 79 g (100 ml) of methyl alcohol and 10 g of benzoyl peroxide were heated for 20 hours with a reflux condenser. The carbon dioxide evolved was absorbed in traps with 40% potassium hydroxide solution. 0.72 g of carbon dioxide was evolved (0.40 mole for 1 mole of the peroxide decomposed). The reaction mixture was distilled, and the fraction distilled off diluted with water. The small amount of benzene that separated was extracted with carbon tetrachloride and nitrated. m-Dinitrobenzene resulted, with m.p. 90°; a mixed sample with known m-dinitrobenzene did not give depression. 0.11 g of m-dinitrobenzene was obtained, which corresponded to 0.05 g of benzene, or 0.01 mole for 1 mole of peroxide decomposed. Formaldehyde content was determined in the aqueous-alcoholic solution by precipitation of the dimedonic derivative; 0.005 g of formaldehyde was found, or 0.004 mole for 1 mole of peroxide. The dimedonic derivative of formaldehyde melted at 187°; a mixed sample with known sample of dimedonic derivative did not give depression. Benzoic acid was determined by titration: 5.84 g was obtained, or 1.16 mole for 1 mole of the peroxide decomposed. A portion of the benzoic acid converted into the methyl ester under the experimental conditions. To determine the total amount of benzoic acid, saponification was carried out on a separate sample, which gave an ester content of 3.15 g or 0.56 mole for 1 mole of peroxide. Thus, the total quantity of benzoic acid constituted 1.72 mole for 1 mole of peroxide decomposed. Benzoic acid melted at 121°; a mixed sample with pure benzoic acid did not give depression.

b) A weighed portion of benzoyl peroxide (3 g) was heated in a sealed tube with methyl alcohol (20 ml) at 120-150° for 20 hours. Benzoic acid determination was carried out by titration. 1.64 g of free benzoic acid was obtained (1.07 mole for 1 mole of peroxide decomposed). Determination of methylbenzoate was carried out by saponification. 0.76 g of methylbenzoate resulted (0.45 mole for 1 mole of peroxide decomposed). The total quantity of benzoic acid was 2.38 g (1.58 mole for 1 mole of peroxide), m.p. 121°; a sample mixed with known benzoic acid did not show depression.

After distilling off the methyl alcohol, benzene was extracted from the distilled fraction, and carbon tetrachloride after dilution with water. m-Dinitrobenzene resulted from nitration, with an m.p. of 90°; a sample mixed with known m-dinitrobenzene did not evidence depression. 0.095 g of m-dinitrobenzene was found, which corresponded to 0.044 g of benzene or 0.04 mole for 1 mole of peroxide decomposed. Formaldehyde was determined in the aqueous-alcoholic solution by precipitation of the dimedonic derivative; 0.005 g or 0.01 mole for 1 mole of peroxide was found. The resulting product melted at 187°; a sample mixed with known dimedonic derivative of formaldehyde did not show depression.

II. Thermal decomposition of benzoyl peroxide in carbon tetrachloride-methyl alcohol mixture. Reaction was carried out in a round-bottomed flask with ground-glass reflux condenser. The reaction mixture was heated on a water bath for 40 hours. In each experiment 50 g of benzoyl peroxide was decomposed in equimolecular amounts of carbon tetrachloride (154 g), and methyl alcohol (32 g). Long before termination of heating, the reaction mixture separated into two layers: upper—aqueous, and lower—nonaqueous. Gases formed during the reaction were absorbed in traps, by 40% KOH solution. The hydrochloric acid content of traps 0.09 g (0.01 mole for 1 mole of peroxide decomposed), was gravimetrically determined. The quantity of CO₂—7.83 g (0.83 mole for 1 mole of peroxide decomposed)—was determined by difference.

The non-aqueous layer was washed with distilled water to remove methyl alcohol and other water-soluble substances, the wash waters being added to the aqueous layer and the volume of the mixture measured. The upper aqueous layer had an acid reaction, the non-aqueous layer a neutral reaction.

The aqueous layer contained formaldehyde, methylal and hydrochloric acid. The formaldehyde was determined by precipitation of the dimedonic derivative—0.42 g (0.07 mole for 1 mole of peroxide decomposed). The quantity of formaldehyde in the free state, and the total quantity of formaldehyde were determined. For

* B. I. Liogonky participated in this work.

determination of the total quantity of formaldehyde, the methylal contained in the aqueous layer was split, by heating the latter in dilute hydrochloric acid with a reflux. 0.45 g of methylal was found (0.03 mole for 1 mole of peroxide decomposed). The dimedonic derivative of formaldehyde melted at 187°; the sample mixed with a known sample of the dimedonic derivative did not show depression. The quantity of hydrochloric acid in the aqueous layer was 3.19 g (0.42 mole for 1 mole of the peroxide decomposed) —determined by titration.

The non-aqueous layer contained carbon tetrachloride, formaldehyde, methylal, chloroform, hexachloroethane, benzoic acid, methylbenzoate and phthalic acid. To split methylal into alcohol and formaldehyde, the non-aqueous layer was heated with dilute hydrochloric acid on a reflux. 3.71 g of methylal, or 0.24 mole for 1 mole of peroxide decomposed, was found. Formaldehyde was determined in the water-acid solution, after rupture of the methylal by precipitation of the dimedonic derivative. 1.48 g, or 0.24 mole for 1 mole of the peroxide decomposed.

By distilling on a fractionating column, a fraction was isolated with a b.p. of 64.5–66°; d_4^{20} 1.5094; n_D^{20} 1.4470. Chloroform was quantitatively determined in it by heating with aniline and alkali [6]. 2.46 g of chloroform resulted, or 0.09 mole for 1 mole of peroxide decomposed. After distilling off the carbon tetrachloride and chloroform, the residue was alkalized and steam distilled. From the non-aqueous distillate layer containing carbon tetrachloride, there was isolated methylbenzoate and hexachloroethane. The non-aqueous layer was fractionated. After distilling off the fraction with b.p. 85–141°, hexachloroethane was isolated from the residue with m.p. 186–187°; a sample mixed with hexachloroethane did not show depression.

Methylbenzoate contained in the filtrate after separation of hexachloroethane was saponified to benzoic acid. 2.92 g (0.1 mole for 1 mole of peroxide decomposed) was found. Hexachloroethane was isolated from the alkaline-alcoholic solution after saponification of the methylbenzoate, and was added to that made earlier in the corresponding experiment. The total quantity of hexachloroethane was 4.30 g (0.09 mole for 1 mole of the peroxide decomposed).

Benzoic acid was isolated by acidification of the alkaline-alcoholic solution, and the hexachloroethane separated melted at 121°; the mixed sample did not show depression.

After termination of the steam distillation, from the alkaline solution in the distilling flask there was isolated a small amount of resin, after which the solution was acidified with dilute hydrochloric acid. A mixture of benzoic and phthalic acids was isolated. Benzoic acid isolated from the mixture melted at 121°; a mixed sample with pure benzoic acid did not show depression. *o*-Phthalic acid was identified by the fluorescein reaction with resorcinol. Benzoic and phthalic acids were determined by titration. 22.65 g (0.9 mole for 1 mole of peroxide decomposed) of benzoic acid and 1.1 g (0.03 mole for 1 mole of peroxide decomposed) were found.

SUMMARY

1. Upon heating with methyl alcohol, benzoyl peroxide reacts with formation of benzoic acid, formaldehyde, benzene and carbon dioxide.

2. Upon heating a mixture of methyl alcohol and carbon tetrachloride in the presence of benzoyl peroxide, there proceeds reaction of the latter with both components. Moreover, a reaction between carbon tetrachloride and methyl alcohol is initiated by the peroxide, with formation of chloroform, formaldehyde and HCl. The direction of the initiated reaction corresponds to the thermal reaction between methyl alcohol and carbon tetrachloride.

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Received July 9, 1952

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THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN SOLVENT MIXTURES: BENZENE AND NITROBENZENE AND NITROBENZENE AND CARBON TETRACHLORIDE

G. A. Razuvaev, B. N. Moryganov and V. A. Stepushkina

It is quite convenient to use benzoyl peroxide for investigation of free radical reactions in the liquid phase, which, as is known from the works of S. Medvedev and co-workers, decomposes into the phenyl- and hydroxybenzoyl radicals [1]. There has appeared lately a number of works devoted to reactions of benzoyl peroxide. It appeared to be of interest to the authors to carry out an investigation of the peroxide decomposition in a mixture of two different solvents in order to determine: 1) whether interaction of peroxide will occur with both components of the mixture, or only one, and 2) whether the secondary radicals forming from the solvents will react with one another. Insofar as the authors are aware, there is practically no such type of work to be found in the literature. For this purpose we have investigated two systems: 1) benzene and nitrobenzene, and 2) nitrobenzene and carbon tetrachloride. It is known [2] that when benzoyl peroxide is heated in benzene, reaction occurs, which is expressed by the following summary equation:



and upon decomposition in nitrobenzene [3]:



There is indication [4] that in the latter case small amounts of diphenyl are obtained. Formation of the latter may be explained by reaction of benzoyl peroxide with benzene, which appears in the reaction mixture in the nature of a side product of the peroxide. During the reaction course in benzene and nitrophenol mixture, which were taken in a 1:1 mole ratio, the following products resulted: CO_2 , benzoic acid, diphenyl and nitrodiphenyls. Thus, it can be seen that interaction of benzoyl peroxide with benzene and nitrobenzene proceeded simultaneously. From the mole ratio of diphenyl to nitrodiphenyls (9:7) it can be seen that the peroxide reacted more readily with benzene.

The second question—whether interaction of secondary free radicals with one another occurred—cannot be answered with the given system, since the final products would be the same in such a reaction. A second system might give an answer to this problem. When benzoyl peroxide interacts with carbon tetrachloride [5], the following reaction proceeds:



Moreover, hexachloroethane results as the result of dimerization of CCl_3 -radicals. The authors obtained the following reaction products: HCl , chlorobenzene, hexachloroethane, nitrodiphenyl, benzoic acid, phthalic acid and also CO_2 . Hence, the benzoyl peroxide reacted simultaneously with both components of the mixture. From the mole ratio of chlorobenzene to nitrodiphenyl (31:6) it can be seen that the peroxide reacted preferably with carbon tetrachloride rather than with the nitrobenzene.

With free CCl_3 - and nitrophenyl- radicals in the system, their combination with one another to form nitrobenzotrichloride could be expected.



However, the authors were unable to find the indicated compound among the reaction products.

EXPERIMENTAL

I. Thermal decomposition of benzoyl peroxide in benzene and nitrobenzene mixture. The reaction

mixture was introduced into a round-bottomed flask equipped with reflux condenser and heated on a water bath. In each experiment 50 g of benzoyl peroxide was decomposed with equimolecular quantities of benzene (78 g) and nitrobenzene (123 g). The carbon dioxide formed during reaction was absorbed in traps containing 40% KOH solution. 13.49 g of CO_2 was found, or 1.48 mole for 1 mole of the peroxide decomposed. Sodium hydroxide solution was added to the reaction products (dark-brown solution) to a weak alkaline reaction, and the mixture was distilled with superheated steam. In the first few liters of distillate, a mixture of benzene and nitrobenzene was collected; in subsequent liters - nitrodiphenyl. The benzene-nitrobenzene mixture (from the distillate) was fractionated and the benzene fraction separated from the nitrobenzene fraction. The nitrobenzene fraction contained diphenyl, for the isolation of which the method of nitrobenzene reduction to aniline by Sn and HCl [4] was used. The diphenyl isolated by this procedure in the amount of 3.06 g (0.09 mole for 1 mole of peroxide decomposed), after recrystallization from alcohol, melted at 68-69°, a mixed sample with pure diphenyl melting at 69°. The nitrodiphenyl distilled with steam, in the amount of 2.93 g, or 0.07 mole for 1 mole of peroxide decomposed, melted at 102-103° before recrystallization. 4-Nitrodiphenyl with m.p. 113° was isolated by recrystallization from methyl alcohol; a sample mixed with pure 4-nitrodiphenyl did not show depression. The residue, after distillation with steam, was acidified with dilute sulfuric acid, the resulting precipitate separated from the solution, dried and sublimed. The sublimed benzoic acid (6.13 g) had an m.p. of 121-121.5°, a sample mixed with pure benzoic acid not giving depression. Upon distilling the reaction products with steam there remained each time in the distilling flask a resin (8.41 g).

II. Thermal decomposition of benzoyl peroxide in nitrobenzene and carbon tetrachloride mixture. Experiments were carried out analogously to the preceding ones. In one experiment, 50 g of benzoyl peroxide was decomposed with equimolecular quantities of carbon tetrachloride (154 g) and nitrobenzene (123 g). The decomposition products (dark brown solution) were alkalized and distilled with superheated steam. From the first few liters of distillate a non-aqueous layer separated, consisting of carbon tetrachloride, chlorobenzene and nitrobenzene mixture, and from subsequent liters - nitrodiphenyls. The carbon tetrachloride, chlorobenzene and nitrobenzene mixture was fractionated, and the carbon tetrachloride, chlorobenzene and nitrobenzene fractions were separated from one another. Upon fractionation of these fractions, a small amount of hexachloroethane with m.p. 186° was isolated; a sample mixed with known hexachloroethane did not show depression.

Chlorobenzene in the amount of 7.82 g, or 0.31 mole for 1 mole of peroxide decomposed, was identified by conversion into p-nitrochlorobenzene by nitration of the chlorobenzene fraction. p-Nitrochlorobenzene recrystallized from methyl alcohol melted at 82°; a sample mixed with known p-nitrochlorobenzene did not give depression.

From the mixture of reaction products, by steam distillation, nitrodiphenyl in the amount of 2.42 g, or 0.06 mole for 1 mole of peroxide decomposed, was isolated. 4-Nitrodiphenyl, with m.p. 113-114°, resulted on recrystallization from methyl alcohol, a mixed sample with known 4-nitrodiphenyl not showing depression.

The alkaline dark-brown solution in the distilling flask after completion of the steam distillation was separated from the resin formed and acidified with dilute sulfuric acid. The resulting precipitate was purified a second time by dissolution in alkali and precipitation by acid. The resulting mixture of benzoic and phthalic acids was separated by recrystallization. 21.12 g, or 0.84 mole for 1 mole of peroxide decomposed, of benzoic acid was found, and 2.30 g of o-phthalic acid, or 0.07 mole for 1 mole of peroxide decomposed. o-Phthalic acid was qualitatively identified by the fluorescein reaction. Benzoic acid was purified by sublimation, and melted at 121.5°; a sample mixed with known benzoic acid did not evidence depression. Nitrobenzoic acids were not found.

Gases formed in the reaction were absorbed in the traps by 40% KOH solution. The HCl content of the traps was 6.68 g, or 0.88 mole for 1 mole of peroxide, determined quantitatively by the gravimetric procedure. The quantity of CO_2 was determined by difference; 8.8 g, or 0.94 mole for 1 mole of peroxide decomposed, was found.

SUMMARY

1. It has been demonstrated that the phenyl radicals formed upon thermal decomposition of benzoyl peroxide in a benzene-nitrobenzene mixture react with both benzene and nitrobenzene. From the ratio of diphenyl and nitrodiphenyl formed, it can be seen that the phenyl radicals preferentially react with benzene, rather than with nitrobenzene.

2. It has been demonstrated that the phenyl radicals formed upon thermal decomposition of benzoyl peroxide in carbon tetrachloride-nitrobenzene mixture react with both of the components of the mixture. From the chlorobenzene and nitrodiphenyl formed, it may be judged that the phenyl radicals preferentially react with carbon tetrachloride rather than with nitrobenzene.

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Received July 9, 1952

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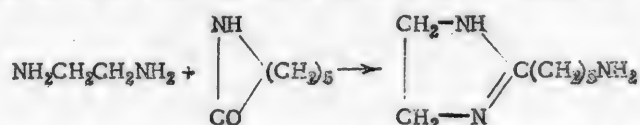


ε-CAPROLACTAM RING OPENING BY ALIPHATIC DICARBOXYLIC ACIDS AND BY AMINES

A. S. Shpitalny, E. A. Meos and K. E. Perepalkin

Some of us have already reported [1] that upon interacting ε-caprolactam with aliphatic dicarboxylic acids, there occurs ε-caprolactam ring opening, with formation of dicarboxylic acids of the $\text{HOOCRCONH}(\text{CH}_2)_5\text{COOH}$ type. The calcium and silver salts of these acids have already been described by the authors.

Since directions in the literature [2] indicated the possibility of rupturing the lactamic bond of ε-caprolactam by amines, the authors made an attempt to obtain interaction products of ε-caprolactam with aniline, hexamethylenediamine and ethylenediamine. The corresponding monamino and diamino derivatives were formed by coupling aniline and hexamethylenediamine with ε-caprolactam in equimolecular ratios. Interaction of ethylenediamine with ε-caprolactam in the same ratio led to formation of the imidazole derivative.



Those indicated amines which were readily soluble in water, alcohol and ether, failed to separate in crystalline form from the reaction mass.

Since it was shown that the benzoyl derivatives of these compounds crystallize well from alcohol-ether solutions, the authors isolated their benzoyl derivatives. Some of the products were also obtained in the form of picrates and oxalates. It was proved by these experiments that in the polymerization-condensation processes taking place in conversion of ε-caprolactam into the polymer [1], interaction of terminal carboxyl and amino groups of the polymer participate, despite the polycondensation reaction.

It also follows from the above-stated that along with the already known methods of synthesis of imidazole derivatives [3], the latter can be obtained by interaction of ethylenediamine with ε-caprolactam.

EXPERIMENTAL

Synthesis of 2-(ε-aminopentyl)-4,5-dihydroimidazole, a conjugation product of ethylenediamine with ε-caprolactam. 1.88 g of ε-caprolactam and 1 g of ethylenediamine (equimolecular ratios) were heated in a sealed tube for 24 hours at 200° in an oil bath. The ampoule was then opened and the reaction mass heated for another hour under vacuum (8 mm) at 150°. Thus, about 10 g of melt was prepared. The benzoyl derivative of the conjugated product was obtained as follows: 1 g of the melt was dissolved in 100 ml of water; 16 ml of 10% sodium hydroxide solution and 3 ml of benzoyl chloride were added. The mixture was shaken 15 minutes, and the white, flaky precipitate formed was filtered off and recrystallized from alcoholic-ether solution.

The benzoyl derivative dissolved readily in alcohol, poorly in water and ether, and had an m.p. of 141°.

Found %: C 72.5, 72.61; H 6.75, 6.67; N 11.46, 11.44. $\text{C}_{22}\text{H}_{35}\text{O}_2\text{N}_3$. Calculated %: C 72.72; H 6.88; N 11.57.

The picrate of the conjugation product was obtained from both alcoholic and aqueous solutions. Its melting point was 190-200° (with decomposition).

Found %: N 21.02, 20.80. $\text{C}_{20}\text{H}_{25}\text{O}_{13}\text{N}_3$. Calculated %: N 20.58.

The picrate of the conjugation product was isolated from alcoholic solution. Upon recrystallizing from alcoholic-aqueous solution, needle crystals, with m.p. 204-206° (with decomposition) precipitated.

Found %: C 38.60, 38.72; H 6.51, 6.55; N 11.29, 11.3. $\text{C}_{13}\text{H}_{20}\text{O}_9\text{N}_3$. Calculated %: C 38.81; H 6.73; N 11.32.

The amount of water of crystallization in the salt was determined by drying the air-dried product at 160° to constant weight (about 1 hour).

Found %: H_2O 10.01, 9.97. $\text{C}_{13}\text{H}_{20}\text{O}_3\text{N}_3 \cdot 2\text{H}_2\text{O}$. Calculated %: H_2O 9.70.

Thus, the oxalate of the conjugation product contained 2 moles of oxalic acid and 2 moles of water.

The analyses given above indicated, accordingly, that the conjugation product of ethylenediamine and ϵ -caprolactam represented 2-(ϵ -aminopentyl)-4,5-dihydroimidazole.

Synthesis of N-(ζ -aminoheptyl)-amide and ϵ -aminocaproic acid, a conjugation product of hexamethylenediamine with ϵ -caprolactam. The given conjugation product and its benzoyl derivative was synthesized in exactly the same manner as the ethylenediamine derivatives described above. The benzoyl derivative of the conjugation product had an m.p. of 118°, soluble in alcohol, insoluble in water and ether.

Found %: C 71.12, 71.2; H 7.9, 8.05; N 9.75, 9.93. $C_{22}H_{35}O_3N_3$ Calculated %: C 71.39; H 8.01; N 9.61.

Thus, the conjugation product of hexamethylenediamine and ϵ -caprolactam satisfies the formula for the N-(ζ -aminoheptyl)-amide of ϵ -aminocaproic acid $NH_2(CH_2)_6NHCO(CH_2)_5NH_2$.

Synthesis of the N-phenylamide of ϵ -aminocaproic acid, a conjugation product of aniline with ϵ -caprolactam. The benzoyl derivative dissolved in alcohol and ether and did not dissolve in water; it was therefore recrystallized from a water-alcohol solution. The benzoyl derivative had an m.p. of 102-103°.

Found %: C 73.40, 73.32; H 6.92, 6.85; N 8.89, 9.30. $C_{19}H_{25}O_2N_2$ Calculated %: C 73.55; H 7.09; N 9.03.

The conjugation product of aniline with ϵ -caprolactam was therefore found to be the N-phenylamide of ϵ -aminocaproic acid $C_6H_5NHCO(CH_2)_5NH_2$.

SUMMARY

1. The interaction products of aniline, hexamethylenediamine and ethylenediamine with ϵ -caprolactam, and their benzoyl derivatives, have been synthesized. Some of these products have also been isolated in the form of picrates and oxalates.

2. It has been demonstrated that imidazole derivatives are formed upon interaction of ethylenediamine with ϵ -caprolactam.

3. Concepts about the character of the reactions which take place during the polymerization-condensation processes involving conversion of ϵ -caprolactam into the polymer have been given.

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Received July 24, 1952.

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*See Consultants Bureau Translation, p. 1311.

THE SYNTHESIS AND CATALYTIC CONVERSION OF β -THIOTETRALOL,

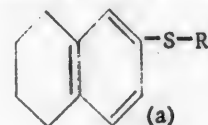
β -TETRALYLNONYLSULFIDE, β -TETRALYLCYCLOHEXYLSULFIDE

AND β -TETRALYLMETHYLSULFIDE OVER ALUMINOSILICATE CATALYST

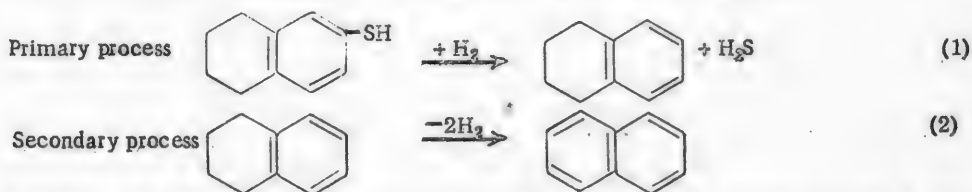
I. N. Tits-Skvortsova and T. A. Danilova

In the works published earlier by the authors [1,2], data are given concerning catalytic conversions over aluminosilicate catalyst of mixed sulfides possessing various structures. Upon the contact of mixed sulfides containing various radicals with catalyst at 300°, rupture of one of the bonds binding sulfur to radicals occurs, and the place of rupture depends upon the nature of the radicals. It has been determined that the bond between the aromatic ring and sulfur is most stable, and in no event does it rupture; however, the bond between sulfur and the naphthene ring is the least stable, and is easily ruptured. It was of interest to study the behavior of those mixed sulfides in which sulfur is bound by one of its valences to a radical composed of a condensed system of aromatic and naphthene rings, which are at two extremes with each other relative to stability of the carbon to sulfur bond. Tetralin, composed of benzene and cyclohexane rings, is such a condensed system.

The purpose of our work was to elucidate whether the hexamethylene ring condensed with the aromatic will effect a rupture of the bond between sulfur and the radicals upon contact of mixed sulfides of the structure (a) with aluminosilicate, and whether in this case the stability of the bond between sulfur and the aromatic ring will be maintained, or whether new mechanisms will appear in the tetralin series.



Synthesized sulfur compounds were passed over aluminosilicate catalyst at 300° under identical conditions. Upon contact of β -thiotetralol with aluminosilicate, there were isolated tetralin (34% of the catalyzate weight), naphthalene (28%), initial β -thiotetralol (7%), 21% of the sulfur contained in the original thiol was trapped as hydrogen sulfide. A small amount of elementary sulfur was contained in the catalyzate, found by shaking a sample of catalyzate with metallic mercury. On the basis of these data, the processes taking place when β -thiotetralol is catalyzed can be expressed by the following schemes:



As a result of destructive hydrogenation, β -thiotetralol converts to tetralin and hydrogen sulfide (a similar reaction also occurs with thiophenols [1,2]). Then, as a result of dehydrogenation of tetralin, naphthalene forms. Up to the present time, dehydrogenation of the hexamethylene ring of sulfur compounds under catalytic conditions has not been observed by the authors. According to the literature data [3,4], more probable seems to be the process of isomerization of the hexamethylene ring of tetralin into pentamethylene, with formation of 1- and 2-methylhydroindene mixture. However, the catalyzate did not contain fractions which corresponded in constants to the isomeric liquid methylhydroindenes. To verify the possibility of dehydrogenating tetralin, the latter was passed over aluminosilicate catalyst under conditions of contact with the sulfur compounds. The catalyzate contained only 1.4 % naphthalene, the rest — tetralin; while naphthalene in the amount of 28% of the catalyzate weight was isolated by catalysis of β -thiotetralol. Such a difference in the amount of naphthalene can be explained by the fact that dehydrogenation of tetralin proceeds not under the influence of aluminosilicate alone, but in addition the elementary sulfur appears to be a dehydrogenating agent. To verify this assumption, tetralin was passed over aluminosilicate with sulfur compounds and simultaneously nitrogen and hydrogen sulfide. (The latter decomposed under the influence of aluminosilicate, to form hydrogen and sulfur, the presence of which were proved both in the catalyzate and used catalyst.) The quantity of naphthalene in the catalyzate increased from 1.4 to 4.6 %. This proved the possibility of dehydrogenation of tetralin, but the process proceeded only to

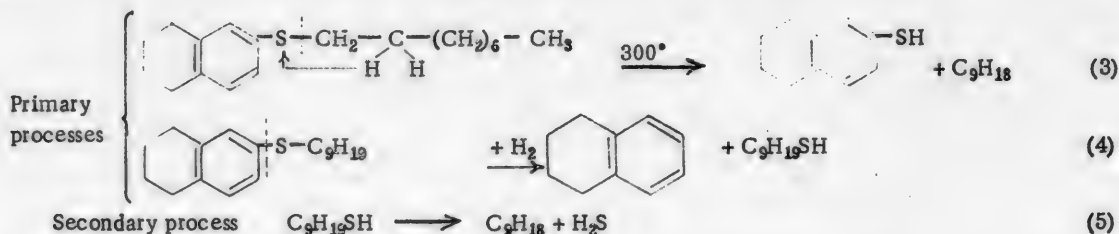
a very small extent. The considerably greater quantity of naphthalene obtained in the catalyzate upon contact of β -thiotetralol might possibly be explained by the fact that the tetralin molecule at its moment of formation from β -thiotetralol can more readily undergo dehydrogenation than the already "primed" molecule.

Dehydrogenation of tetralin under the influence of sulfur has been described in the literature [3,5,6]. In the process, which is non-catalytic, the hydrogen evolved combines with sulfur to give hydrogen sulfide. The possibility of this process in the authors' case is confirmed by the absence of hydrogen in the gas evolving upon catalysis of β -thiotetralol: upon catalytic dehydrogenation of tetralin, the gas evolved should have contained hydrogen.

Somehow or other, a new phenomenon has been observed — dehydrogenation of the hexamethylene ring of tetralin with formation of naphthalene — upon passage of β -thiotetralol over aluminosilicate.

From the catalyzate obtained, there were separated from β -tetralylnonylsulfide: tetralin (27% of the catalyzate weight), nonene-1 (16%), β -thiotetralol (3%), naphthalene (4%), and nonylmercaptan (4%). 19% of the sulfur contained in the original sulfide was trapped as hydrogen sulfide.

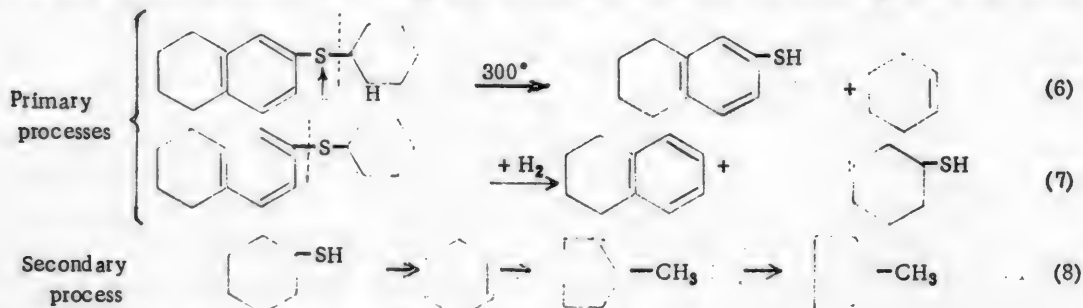
It could have been assumed that the following process might proceed upon catalysis of β -tetralylnonylsulfide:



and, moreover, that the secondary processes would proceed according to Equations (1) and (2).

If rupture of the sulfide molecule occurs between the sulfur and the alkyl (Scheme 3), then β -thiotetralol and nonene-1 should be formed; in the case of bond rupture between sulfur and the tetralin radical (Equation 4), tetralin and nonylmercaptan should be formed. But inasmuch as tetralin and nonene may form as the result of secondary processes (Equations 1 and 5*), their presence in the catalyzate is not proof of the accuracy of Equations 3 and 4). The point at which the sulfide molecule ruptures is determined by the thiols which are found to be primary products. All possible compounds foreseen by the above-given equations have been separated from the catalyzate, among them both thiols. Hence, rupture of the β -tetralylnonylsulfide molecule occurred at both valence points of the sulfur — this phenomenon also being observed for the first time upon catalysis of sulfur compounds over aluminosilicate. Concerning the quantitative aspect of the process, nothing can be said, since the relation of primary substances is obscured as a result of the secondary reactions which take place. It should be noted that upon contact of this sulfide with aluminosilicate, the dehydrogenation of tetralin to naphthalene may perhaps proceed more readily, since, according to [6], the role of the dehydrogenating agent may be played by sulfur itself.

Upon contact of β -tetralylcyclohexylsulfide with aluminosilicate, a catalyzate resulted, from which was isolated tetralin (28% of the catalyzate weight), β -thiotetralol (18%), methylcyclopentane (17%), naphthalene (7%), and the initial sulfide (3%). Sulfur, in the form of hydrogen sulfide, was obtained in amount equal to 28% of the weight of initial sulfide. By analogy with β -tetralylnonylsulfide, the following course can be offered:



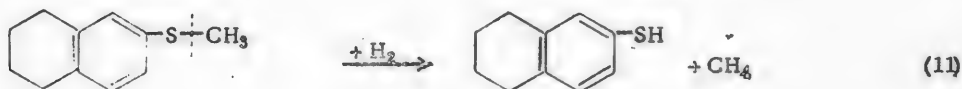
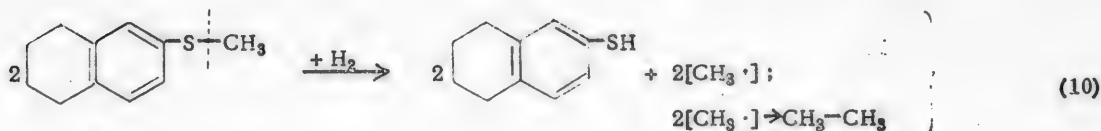
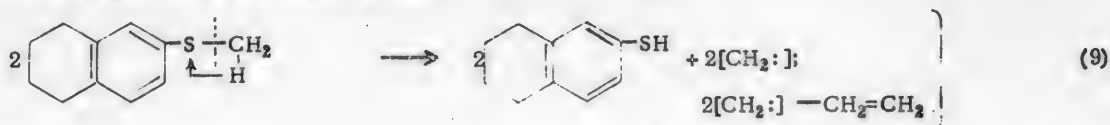
and secondary processes, proceeding according to Equations (1) and (2).

* Concerning conversion of aliphatic mercaptans into alkenes and hydrogen sulfide, see the earlier published work [1].

The presence of β -thiotetralol has indicated that bond rupture occurs between sulfur and the cyclohexane ring. The cyclohexane formed changes further, according to Equation (8), converting completely into methylcyclopentane, which was isolated from the catalyze. The possibility of conversion of cyclohexane into methylcyclopentane under conditions of contact with sulfur compounds was proved earlier by the authors [7]. The absence of cyclohexanethiol in the catalyze does not indicate that bond rupture between sulfur and tetralin does not occur; the possibility exists that such a rupture has occurred, and that the cyclohexanethiol formed has converted into methylcyclopentane according to Equation (8)*; however, it could not be proved in the case given. Consequently, in the case of β -tetralylcyclohexylsulfide, bond rupture between the cyclohexane ring and sulfur was proved, and was accompanied by disproportionation of hydrogen.

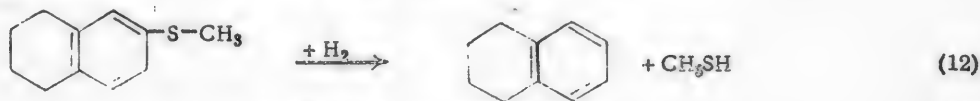
Of special interest was conversion of β -tetralylmethylsulfide, where the simplest radical, methyl, was bound by one of the sulfur valences. As is known, a compound containing the methyl group differs in its composition from the higher homologs in certain characteristic properties. It was reasonable to expect the same peculiarity from β -tetralylmethylsulfide as well.

Upon contact with aluminosilicate, the following course for the processes could be assumed. In the case of bond rupture between sulfur and methyl groups



and processes proceeding according to Equations (1) and (2).

In the case of bond rupture between sulfur and the tetralin nucleus:



and the processes according to Equation (2).

Equation (9) reflects a characteristic for the reaction of aliphatic-aromatic sulfides, with bond rupture between sulfur and the alkyl and disproportionation of hydrogen. The specificity of the given case lies in the fact that the alkene which is formed, methylene, is unable to exist. Therefore, the ethylene present in the outgoing gases could be presumed to have been formed as the result of combination of the methylene with itself. The reaction course according to Equation (10) could lead to formation of ethane via the methyl radical stage. In the case of destructive hydrogenation (Equation 11), the methyl radical should convert to methane. Bond rupture between sulfur and alkyl according to any of these equations leads to formation of β -thiotetralol, which converts into tetralin and naphthalene, as the result of a secondary process (Equations 1 and 2). Rupture between sulfur and the tetralin radical (Equation 12) would give methyl mercaptan and tetralin, which, as a result of secondary processes (Equations 13 and 2) could convert into dimethyl sulfide and naphthalene.

As the result of contact of β -tetralylmethylsulfide with aluminosilicate, there were isolated from the catalyze tetralin (35% of the catalyze weight), naphthalene (36%), dimethylsulfide (15.6%), and β -thiotetralol (6%). Methyl mercaptan was trapped out of the exit gases, in the amount of 1.5% sulfur of the original weight of sulfide, and hydrogen sulfide (5.6% sulfur). Analysis of the gas freed from hydrogen sulfide and methyl mercaptan indicated that the hydrocarbons present contained only a trace of methane. There was no ethylene or ethane. The following conclusions could be drawn from these data: inasmuch as the outgoing gases did not contain ethane and ethylene, Equations (9) and (10) do not correspond to actuality. The presence of four possible primary

* Conversion of cyclohexanethiol into methylcyclopentane was described in an earlier published work [1].

reaction products — β -thiotetralol, methane, tetralin, and methyl mercaptan — in the liquid catalyzate and in the gases, indicated that the process proceeds simultaneously according to both Equation (11) and Equation (12). Hence, in the case of β -tetralylmethylsulfide, molecular rupture occurs at both of the sulfur bonds with radicals, similarly to that found above for β -tetralylnonylsulfide. The presence of naphthalene, dimethylsulfide, and hydrogen sulfide, which appeared to be secondary reaction products, indicated a further change of the primary reaction products according to Equations (1), (9), and (13)*. The course of the destructive hydrogenation reaction upon rupture of the bond between sulfur and alkyl (Equation 11) has been observed for the first time by the authors; in this fact the specificity of conversion of sulfides containing a methyl radical over aluminosilicate is inherent. The reaction proceeds according to Equation (11), since it cannot proceed by the usual scheme for aliphatic-aromatic sulfides.

EXPERIMENTAL

The synthesized sulfur compounds were passed over aluminosilicate under identical conditions. 23 g of catalyst was placed in a reaction tube, 1.5 cm in diameter. Length of the catalyst layer was 30 cm. The volumetric rate at which the substance was passed over catalyst was 0.25. In all experiments the reaction was carried out at 300° in a gentle stream of nitrogen. Evolution of hydrogen sulfide was observed in all cases; the hydrogen sulfide was trapped by sodium plumbite. The catalyst was regenerated after each experiment by passing a strong stream of air through at 500°. The air was then displaced with nitrogen. As a control experiment indicated, the presence of oxygen in the outgoing gas during catalysis is explained by incomplete displacement of air from the apparatus.

The catalyzates were fractionated many times for the purpose of isolating individual compounds from them. In each case, apart from the fractions corresponding to individual compounds, a certain amount of tar resulted. No lower cracking fractions were observed. Repeated fractionation of the catalyzate fractions led to some loss of substance. Therefore, the percentage ratios of substances isolated from the catalyzate cannot be considered as accurate, but only qualitatively characteristic of the catalyzate composition.

In order to prove that changes occurring with sulfides over aluminosilicate catalyst are not the result of thermal decomposition, β -tetralylcyclohexylsulfide was passed through an empty catalysis tube at 300° in a stream of nitrogen, i.e., under the conditions of catalysis, but without catalyst. In this case unchanged β -tetralylcyclohexylsulfide was obtained.

β -Thiotetralol resulted from reduction of β -tetralin sulfochloride [8], which was synthesized by interaction of tetralin with chlorosulfonic acid [9]. The yield of β -tetralinsulfochloride was 53% of theoretical. M.p. 54-56°. Literature data: m.p. 58° [9]. The yield of β -thiotetralol was 75.4% of theoretical. B.p. 141° (12 mm); 135° (8 mm); n_D^{20} 1.5972; d_4^{20} 1.0898. Literature data: b.p. 146-148° (14 mm) [8].

Found %: C 73.04, 73.09; H 7.45, 7.40; S 19.39, 19.40. $C_{10}H_{12}S$. Calculated %: C 73.12; H 7.36; S 19.52.

17.8 g of β -thiotetralol was passed over aluminosilicate catalyst. Weight of the resulting catalyzate was 11.8 g (66% of the thiol weight). The hydrogen sulfide evolved during catalysis was precipitated with sodium plumbite. Weight of the resulting PbS was 5.5 g, which corresponded to 0.74 g of sulfur (21.3% of the sulfur weight in initial thiol). A large amount of elementary sulfur was found in the catalyzate by shaking with metallic mercury. Tetralin, naphthalene, and the initial β -thiotetralol were isolated from the catalyzate. The weights and constants for the compounds isolated are given in Table 1.

After removal of hydrogen sulfide, the outgoing gas contained CO_2 0.2%; O_2 1.1%; saturated compounds, 0.3%. The remainder — nitrogen, in a stream of which the experiment was carried out.

β -Tetralylnonylsulfide was synthesized for the first time by the general method of sulfide synthesis [10] from β -thiotetralate and nonyl bromide. The yield of β -tetralylnonylsulfide was

TABLE 1
Catalysis of β -Thiotetralol

Substance isolated from catalyzate	Weight		Melting point (°C)	Boiling point	n_D^{20}	d_4^{20}
	(in g)	in % of catalyzate wt.				
Tetralin **	4.0	33.9	—	77.5-78.5° (6 mm)	1.5445	0.9703
Naphthalene ***	3.3	27.9	80	—	—	—
β -Thiotetralol	0.8	6.8	—	122° (4 mm)	1.5990	1.0901

* Conversion of aliphatic mercaptans into the corresponding sulfide is described in a work published earlier by the authors [1].

** Literature data: b.p. 90.8-91.2° (17 mm) [11]; n_D^{20} 1.5438 [12]; d_4^{20} 0.9707 [12].

*** Naphthalene picrate m.p. 150°. Literature data: naphthalene, b.p. 80.4° [13]; naphthalene picrate m.p. 149-149.5° [4].

41 g (68% of theoretical); b.p. 218.5-219.5° (4 mm); n_D^{20} 1.5370; d_4^{20} 0.9671.

Found %: C 78.70, 78.66; H 10.88, 10.82; S 10.46, 10.50. $C_{10}H_{10}S$. Calculated %: C 78.57; H 10.41; S 11.02.

30.0 g of β -tetralylnonylsulfide was passed over aluminosilicate catalyst. 20.9 g of liquid catalyzate was obtained (69.7% of the sulfide weight). The hydrogen sulfide evolved during catalysis gave 4.8 g of PbS, which corresponded to 0.64 g of sulfur (19.3% of the weight of sulfur in the original sulfide). From the catalyzate nonene-1, nonyl mercaptan, tetralin, naphthalene, and β -thiotetralol were separated. Nonyl mercaptan and tetralin, usually unseparable by ordinary fractionation because of the proximity of their boiling points, were separated from one another by precipitating the mercaptan with an alcoholic solution of sodium plumbite and then filtering the precipitate of $(C_9H_{19}S)_2Pb$. Tetralin was separated from the filtrate and from the lead nonyl mercaptide, by acidification with hydrochloric acid, the nonyl mercaptan was regenerated. The weights and constants of the compounds precipitated are given in Table 2.

TABLE 2

Catalysis of β -Tetralylnonylsulfide

Substances separated from the catalyzate	Weight		Melting point	Boiling point	n_D^{20}	d_4^{20}
	(in g)	(in % of catalyzate wt.)				
Tetralin*	5.5	26.8	—	97.5-100.5° (20 mm)	1.5442	0.9687
Nonene-1**	3.3	15.7	—	146-150 (756 mm)	1.4120	0.7267
β -Thiotetralol***	2.6	12.4	—	136 (8 mm)	1.5985	1.0890
Naphthalene****	0.9	4.3	80°	—	—	—
Nonylmercaptan*****	0.8	3.8	—	101.5-102.5 (20 mm)	1.4555	0.8420

* Literature data: see annotations to Table 1.

** Literature data: b.p. 146° [15]; n_D^{20} 1.4169; d_4^{20} 0.7296 [16].

*** See above for β -thiotetralol.

**** Literature data: see annotations to Table 1. The naphthalene picrate had m.p. 150°.

***** Literature data: b.p. 91.9-92.4° (10 mm); n_D^{20} 1.4537; d_4^{20} 0.84015 [17].

Synthesis of β -tetralylcyclohexylsulfide. An attempt to synthesize β -tetralylcyclohexylsulfide, not described in the literature, from the potassium derivative of β -thiotetralol and cyclohexylbromide gave poor results: yield did not exceed 27% due to a side reaction of cyclohexane formation from cyclohexylbromide under the influence of alkali. A series of experiments was set up for the purpose of increasing the sulfide yield, in which initial substances, temperature conditions, heating time were varied. β -Thiotetralol, alkali, and halide were taken in equimolecular quantities. The experimental results are given in Table 3.

TABLE 3

Synthesis of β -Tetralylcyclohexylsulfide

No.	Quantity of initial β -thiotetralol (g)	Alkali	Halide	Temperature of experiment	Heating time (in hours)	β -Tetralylcyclohexylsulfide	
						Yield (% of theoretical)	n_D^{20}
1	20	KOH	$C_6H_{11}Br$	60-80°	1.5	25.0	1.5803
2	80	KOH	$C_6H_{11}Br$	75-86	2.0	27.0	1.5804
3	20	NaOH	$C_6H_{11}Br$	75-85	2.0	32.5	1.5797
4	53	NaOH	$C_6H_{11}Br$	68-75	2.0	30.3	1.5805
5	20	KOH	$C_6H_{11}Cl$	85-95	3.0	18.9	1.5802
6	10	KOH	$C_6H_{11}Cl$	118-123	6.0	31.6	1.5805
7	24	NaOH	$C_6H_{11}Cl$	115-124	10.0	34.9	1.5812

A maximum yield of β -tetralylcyclohexylsulfide (35%) was obtained by heating cyclohexylchloride with sodium thiotetralate for 10 hours at 115-123°. Cyclohexene formation in larger or smaller amounts was observed in all experiments. The resultant β -tetralylcyclohexylsulfide was redistilled in vacuo; b.p. 187.5-188.5° (3 mm); n_D^{20} 1.5800; d_4^{20} 1.0543.

Found %: C 78.28, 78.11; H 8.95, 8.96; S 13.03, 12.94. $C_{16}H_{22}S$. Calculated %: C 77.99; H 9.00. S 13.01.

40.4 g of β -tetralylcyclohexylsulfide was passed over aluminosilicate catalyst. 33.0 g of catalyzate was obtained (81.7% of the sulfide weight). Hydrogen sulfide from the outgoing gases gave 11.0 g of PbS, which corresponded to 1.47 g of sulfur (27.95% sulfur of the original sulfide weight). Upon fractionating the catalyzate, the

following low boiling fractions were isolated: 1) b.p. 72-74°, n_D^{20} 1.4138; 2) b.p. 75-76°, n_D^{20} 1.4230. These fractions were apparently a mixture of three closely-boiling hydrocarbons: methylcyclopentane (b.p. 72.0-72.2°, n_D^{21} 1.4088 [18]), 1-methylcyclopentene-1 (b.p. 75-76°, n_D^{20} 1.4270 [19]), and 1-methylcyclopentene-2 (b.p. 69°, n_D^{20} 1.4222 [20]). The fractions did not contain sulfide. To determine the amount of unsaturated compounds, the iodine numbers of the fractions were determined. The iodine number for the first fraction was equal to 38.3; the percentage unsaturation was 12.52. The iodine number for the second fraction was equal to 68.3; the percentage unsaturation was 22.29. Hence both fractions contained a negligible amount of methylcyclopentene. Both fractions were combined and treated with an equal volume of 90% sulfuric acid. Upon distillation of the residue, methylcyclopentane resulted. Tetralin, naphthalene, β -thiotetralol, and the initial β -tetralylcyclohexylsulfide were separated by fractionation of the higher-boiling portions of the catalyzate. The weights and constants for the compounds obtained are given in Table 4.

TABLE 4

Catalysis of β -Tetralylcyclohexylsulfide

Substance isolated from catalyzate	Weight		Melting point	Boiling point	n_D^{20}	d_4^{20}
	(in g)	(in % of catalyzate weight)				
Tetralin *	9.2	27.88	—	74-75° (4 mm)	1.5465	0.9700
β -Thiotetralol *	6.1	18.48	—	135° (8 mm)	1.5985	1.0889
Methylcyclopentane **	5.51	16.69	—	72.5-73.5°	1.4119	0.7413
Naphthalene *	2.3	6.96	80°	—	—	—
β -Tetralylcyclohexylsulfide	1.0	3.03	—	—	1.5818	—

* Literature data — see annotation to Tables 1 and 2. Naphthalene picrate had m.p. 150°.

** Literature data: b.p. 72-72.2°; n_D^{21} 1.4088; d_4^{21} 0.7474 [18].

TABLE 5

Catalysis of β -Tetralylmethylsulfide

Substance isolated from the catalyzate	Weight		Melting point	Boiling point	n_D^{20}	d_4^{20}
	(in g)	(in % of catalyzate weight)				
Tetralin *	8.0	34.63	—	77.5° (8 mm)	1.5445	0.9712
Naphthalene *	8.4	36.36	80°	—	—	—
Dimethylsulfide **	3.6	15.58	—	33-39°	1.4418 (at 13.5°)	0.8534 (at 13.5°)
β -Thiotetralol *	1.3	5.63	—	136° (8 mm)	1.5990	1.0903

* Literature data: see annotation to Tables 1 and 2. Naphthalene picrate had a m.p. of 149.5°.

** Literature data: b.p. 37.2°; d_4^{20} 0.8449 [24].

β -Tetralylmethylsulfide was synthesized from potassium β -thiotetralate and methyl iodide [10]. The yield of β -tetralylmethylsulfide was 74.67 % of theoretical. B.p. 155° (12 mm); n_D^{20} 1.5920; d_4^{20} 1.0711. Literature data: b.p. 158-159° (10 mm) [21].

32 g of β -tetralylmethylsulfide was passed over aluminosilicate catalyst. The catalyzate weight was 31 g (74 % of the sulfite weight). The exit gases contained hydrogen sulfide and methyl mercaptan, separated by selective precipitation in the form of $(CH_3S)_2Pb$ and CdS [22]. The resulting mercaptide gave a positive reaction for CH_3SH with concentrated H_2SO_4 , and with isatin a green coloration [23]. CdS was converted into PbS . 2.4 g of PbS was obtained, which corresponded to 0.34 g of H_2S , or 0.32 g of sulfur (5.56% sulfur of the original sulfide); and 6.7 g of $(CH_3S)_2Pb$, which corresponded to 1.07 g of CH_3SH or 0.71 g of sulfur (12.36% sulfur weight of original sulfide). Dimethylsulfide, tetralin, naphthalene, and β -thiotetralol were separated from the catalyzate. Tetralin and β -thiotetralol contained considerable elementary sulfur, which was removed with metallic mercury. The weights and constants of the substances synthesized are given in Table 5.

The dimethylsulfide gave a clear-cut positive reaction for sulfur sulfide with mercurous nitrate. The outgoing gas (1600 ml) from the catalysis contained 4.4% O_2 and 0.7% saturated compounds, after removal of the hydrogen sulfide. The remainder was nitrogen, in a stream of which catalysis was carried out. Upon calculating the n number for the formula of a saturated hydrocarbon C_nH_{2n+2} , it was found that $n = 1$. The gas contained only traces of methane, less than 1%. There was no ethane in the gas. The number, n , for the formula of saturated hydrocarbons was calculated in the following manner: from each milliliter of saturated hydrocarbon C_nH_{2n+2} there results on combustion n ml of CO_2 . Hence, $n = \frac{\Delta CO_2}{\Delta V}$, where ΔCO_2 = the volume of carbon dioxide obtained on burning saturated hydrocarbons; ΔV = the volume of saturated gases taken for combustion.

The behavior of tetralin over aluminosilicate catalyst was studied for an explanation of the catalytic conversion mechanism.

30.0 g of tetralin (b.p. 81.5-82.5° (8 mm); n_D^{20} 1.5412; d_4^{20} 0.9671) was passed over aluminosilicate under catalytic conditions of the sulfur compounds. 29.2 g of catalyzate resulted (97.33% of the tetralin weight). The catalyzate was cooled with solid carbon dioxide, and the naphthalene which separated out on the funnel at -13° was filtered. At this temperature the tetralin melted and went into the filtrate, naphthalene remaining on the filter. 0.4 g of naphthalene was isolated with m.p. of 80°. The yield of naphthalene constituted 1.4% of the catalyzate weight. The exit gas contained 0.9% CO_2 ; unsaturated compounds: 0.3% O_2 , 1% CO , 0.3% H_2 , 0.1% saturated (C_nH_{2n+2}) 2.9%. Saturated hydrocarbon-methane ($n = 1$). The remainder was nitrogen, in a stream of which the experiment was carried out. Thus, the gas contained about 3 volume percent of methane and traces of remaining gases.

19.9 g of tetralin was passed over aluminosilicate catalyst under catalytic sulfur conditions in a stream of nitrogen mixed with hydrogen sulfide. By double freezing of the catalyzate with solid carbon dioxide, with subsequent filtration at -13°, 0.9 g of naphthalene was isolated, which constituted 4.64% of the catalyzate weight. M.p. 80°. Thus, the presence of hydrogen sulfide facilitated dehydrogenation of the tetralin.

For clarification of the thermal stability of the β -tetralin series of sulfides, 19.6 g of β -tetralylcyclohexylsulfide (n_D^{20} 1.5792, d_4^{20} 1.0521) was passed through empty catalytic tubes in a stream of nitrogen at 300°. 19.0 of catalyzate resulted (96.94% of the sulfide weight) whose constants coincided with the constants of the sulfides investigated (n_D^{20} 1.5794, d_4^{20} 1.0527).

SUMMARY

1. β -Thiotetralol, upon contact with aluminosilicate at 300°, converts into tetralin, naphthalene, and hydrogen sulfide. Naphthalene forms by dehydrogenation of tetralin. The phenomenon of dehydrogenation of the hexamethylene ring to the benzene ring under the conditions of contact with sulfur compounds has been observed for the first time.
2. Upon contact of β -tetralynonylsulfide and β -tetralylmethylsulfide with aluminosilicate, there occurs rupture of the molecule at both valences which bind sulfur to the radicals. With aliphatic-aromatic sulfides under identical conditions, the bond between sulfur and alkyl, only, is ruptured. Weakening of the bond between the benzene ring and the sulfur in β -tetralino-aliphatic sulfides can be explained by the effect of the hexamethylene ring which is condensed with benzene in the tetralin molecule.
3. Alkenes form from aliphato-tetralin and aliphato-aromatic sulfides upon their contact with aluminosilicate as a result of hydrogen disproportionation. β -Tetralylmethylsulfide represents an exception: upon rupture of the bond between methyl and sulfur, there has been observed for the first time destructive dehydrogenation with sulfides of this type, which is related to the impossibility of existence of methylene.
4. Rupture of the bond between sulfur and the hexamethylene nucleus has been proved for β -tetralylcyclohexylsulfide, analogous to the behavior of naphthene-aromatic sulfides.

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Received March 3, 1953.

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RESEARCH IN THE FIELD OF AMINO ACIDS

V. THE CONDENSATION REACTION OF ALDEHYDES AND KETONES WITH ACYLGLYCINES

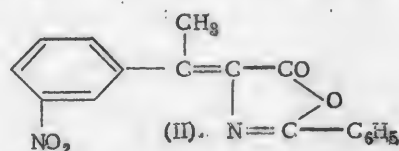
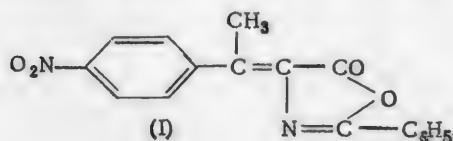
S. I. Lurye, E. S. Chaman, and G. A. Ravdel

Numerous investigations on the condensation reaction of aldehydes with acylglycines (the Erlenmeyer reaction) have indicated that the character of the aldehyde radical affects the course of this reaction. Aromatic aldehydes and a majority of the heterocyclic aldehydes enter readily into reaction with hippuric acid to form oxazolones in good yields [1]. Aldehydes of the aliphatic series react with difficulty with hippuric acid [2], and under analogous conditions, do not react with aceturic acid. Of the aliphatic-aromatic aldehydes, phenylacetaldehyde and phenylpropionic aldehyde do not react with hippuric acid [3]. The nature of the substituents in the ring of aromatic aldehydes apparently does not affect the direction of the reaction (as distinguished from the Perkin reaction). There are characteristic indications for the fact that the presence of a nitro group in the ortho position to the aldehyde group in some cases lowers, and in others increases, the yield of oxazolone. Thus, upon condensing 2-nitro-3,4-methylenedihydroxybenzaldehyde with hippuric acid, the yield of oxazolone was 35-42% [4], while condensation of 3,4-methylenedihydroxybenzaldehyde with hippuric acid resulted in a 67% yield of the oxazolone [5], or 82% [6]; oxazolone resulted in 84% yield [7] from 2-nitro-5-methoxybenzaldehyde, while the yields of corresponding oxazolones from the methoxybenzaldehydes did not exceed 80%.

Evidently, in the cases indicated, reaction conditions for the condensation have an effect, but not the presence of the nitro-group. The condensation reaction of o-nitrobenzaldehyde with hippuric acid can serve as an example to confirm the effect of reaction conditions upon the yield of oxazolone. According to the literature data, 2-phenyl-4-(2-nitrobenzylidene)-5-oxazolone results in 60% yield [8], or 61.2% [7]. But when this reaction was carried out by the authors under other conditions, i.e., using potash in place of sodium acetate (see Experimental), the same oxazolone then resulted in 80-85% yield.

A study of the condensation reaction of ketones with hippuric acid has indicated a somewhat different relation between the ketone radical structure and its ability to enter into a condensation reaction with hippuric acid. Acetone [9], methylethylketone [10], cyclohexanone [11], and benzylideneacetone [12] react with hippuric acid to form the oxazolones in yields of 73, 67, 49, and 46% respectively. It is apparently impossible to increase the yields, due to the existence of a supra-acylation process which occurs simultaneously with the condensation process. Upon condensing acetone and methylethylketone with hippuric acid, sodium benzoate was obtained in the amount of 20-30% of the hippuric acid taken.

Attempts were made to obtain the oxazolone of acetophenone [11], but it was found that acetophenone does not react with hippuric acid. The author also studied the possibility of condensing acetophenone with hippuric acid under various conditions; during this time several compounds were synthesized, among them 2-phenyl-4-(1'-hydroxyethylidene)-5-oxazolone, but the oxazolone sought for was not found. It appeared of interest to the authors to verify the effect of the nitro group in the molecule of aliphatic-aromatic ketone upon the ability of the carbonyl group to enter into reaction with hippuric acid. For this purpose, experiments were set up for condensing p- and m-nitroacetophenone with hippuric acid. In both cases, the corresponding oxazolones resulted - (I) and (II).



wherein 2-phenyl-4-[1'-(p-nitrophenyl)ethylidene]-5-oxazolone (I) was isolated in two crystalline modifications - red and yellow. The yellow-colored crystals were the stable form; the red-colored crystals dissolved in organic solvents to precipitate as the yellow crystals.

As indicated above, aldehydes of the aliphatic series entered, with difficulty, into condensation reaction with hippuric acid, and polymerization products resulted along with the oxazolone. Various investigators have changed the Erlenmeyer reaction conditions for the purpose of eliminating the polymerization reaction and of increasing the yield of oxazolone. One of them [13] used lead acetate in place of sodium acetate, while others did not introduce all of the aldehyde at once into the reaction medium, but instead added it gradually, dropwise, eliminating in this way prolonged contact of aldehyde with the reaction medium. Both modifications give positive results.

On the basis of accumulated research material on the Erlenmeyer reaction, investigators have come to the conclusion that reaction proceeds through the formation of 2-phenyl-5-oxazolone, and not through formation of the unsaturated acylated amino acid. When hippuric acid undergoes cyclization into 2-phenyl-5-oxazolone, there is formed acetic acid, which changes the pH of the medium, which perhaps facilitates polymerization of aldehydes in the aliphatic series. Sodium acetate does not seem to be a sufficiently good buffer under the conditions of acetic acid formation, and when substituted by lead acetate, or when the effect of acetic acid on the aldehyde was removed by a gradual introduction of the latter into the reaction medium, there was then obtained from acetaldehyde 2-phenyl-4-ethylidene-5-oxazolone in 47-60% yield, and from isobutyraldehyde 2-phenyl-4-isobutylidene-5-oxazolone in 31% yield [13] instead of 8%.

The method proposed in 1950 [6] for synthesizing oxazolones by using potash in place of sodium acetate increased by 10-15% the yields of oxazolones from aromatic aldehydes. Apparently, in the case of aromatic aldehyde condensations with acylglycines, acetic acid affects this process unfavorably. However, in the presence of potash, the acetic acid is neutralized, and the yields of oxazolones are therefore greater than when sodium acetate is used. The reaction of aromatic aldehydes with hippuric acid in the presence of potash begins at room temperature, and is then accompanied by evolution of heat, whereupon the temperature changes sharply, depending upon the character of the aldehyde. Aromatic aldehydes react with aceturic acid upon heating, but the oxazolones are not always obtained in good yields. Benzaldehyde reacts with hippuric and with aceturic acids with good yields (Table 1). However, substituted benzaldehydes, with aceturic acid, do not always produce oxazolones in good

TABLE 1

Oxazolone	Formula	Yield of oxazolone (in %) in the presence of:		
		CH ₃ COONa	K ₂ CO ₃	NaHCO ₃
2-Phenyl-4-benzylidene-5-oxazolone	C ₁₆ H ₁₁ O ₂ N	66	83.7	83.5
2-Methyl-4 benzylidene-5-oxazolone	C ₁₁ H ₉ O ₂ N	77	85	72.7-78
2-Phenyl-4 (p-methoxybenzylidene)-5-oxazolone	C ₁₇ H ₁₃ O ₃ N	80	80-85	85
2-Methyl-4 (p-methoxybenzylidene) 5-oxazolone	C ₁₂ H ₁₁ O ₃ N	35-45	40-50	25-30
2-Phenyl-4 (o-nitrobenzylidene)-5-oxazolone	C ₁₆ H ₁₀ O ₄ N ₂	60	85	82
2-Methyl-4 (o-nitrobenzylidene)-5-oxazolone	C ₁₁ H ₉ O ₄ N ₂	—	—	20
2-Phenyl-4-isopropylidene-5-oxazolone	C ₁₂ H ₁₁ O ₂ N	62.7	—	50-56
2-Phenyl-4-isobutylidene-5-oxazolone	C ₁₃ H ₁₃ O ₂ N	8	21	26
2-Phenyl-4-[1' phenylethylidene]-5-oxazolone	C ₁₇ H ₁₃ O ₂ N	0	0	0
2-Phenyl-4 [1' (p-nitrophenyl)-ethylidene]-5-oxazolone	C ₁₇ H ₁₂ O ₄ N ₂	—	28	31
2-Phenyl-4 [1' (m-nitrophenyl)-ethylidene]-5-oxazolone	C ₁₇ H ₁₂ O ₄ N ₂	—	13-15	—

yields. From p-methoxybenzaldehyde and aceturic acid, oxazolone results in maximum yield of 50%. It was of interest to the author to clarify the influence of a nitro group in the aldehyde molecule upon its condensation with aceturic acid. As indicated above, o-nitrobenzaldehyde reacted with hippuric acid to give the oxazolone in 80-85% yield. The reaction of o-nitrobenzaldehyde with aceturic acid has not been described in the literature.

In this connection the author set up o-nitrobenzaldehyde condensation experiments with aceturic acid, and 2-methyl-4(o-nitrobenzylidene)-5-oxazolone resulted in 20-25% yield. A study of this oxazolone indicated that it differed somewhat in its properties from the other oxazolones. It was readily hydrolyzed by alkali in the cold, and also reacted in the cold with aniline (or piperidine) to give the corresponding anilide (or piperidide). Upon recrystallization of technical oxazolone from alcohol, there was isolated, along with the oxazolone, the oxazolone acid and its ethyl ester. It is possible that instability of the oxazolone ring is the reason for the poor yield of oxazolone.

The author studied the condensation reaction of aldehydes and ketones with acylglycines in the presence of

sodium bicarbonate, obtaining almost the same yields as when potash was used. In Table 1 the oxazolone yields, using potash and sodium bicarbonate, are given. With potash the reaction proceeded at room temperature, and with sodium bicarbonate, at 40-50°.

In the study of Erlenmeyer's reaction, the author noted the ability of saturated and unsaturated acylated amino acids to yield readily crystallizable salts with bases. The author obtained several quaternary ammonium salts of acylamino acids with piperidine (Table 2).

TABLE 2

Acylamino acid	Formula of the quaternary ammonium salt	Melting point	% N	
			Found	Calculated
Acetylleucine	$C_{13}H_{25}O_3N_2$	146-147°	10.84	10.51
Acetylvaline	$C_{12}H_{23}O_3N_2$	108-111	11.05	11.15
α -Benzoylamino cinnamic acid	$C_{21}H_{21}O_3N_2$	153-154	7.95	8.26
α -Acetylamino cinnamic acid	$C_{16}H_{22}O_3N_2$	152-153	9.65	9.24
α -Benzoylamino- β -isopropylacrylic acid	$C_{19}H_{25}O_3N_2$	109-116	7.90	7.86
α -Acetylamino-p-methoxycinnamic acid	$C_{17}H_{21}O_4N_2$	181-182	8.71	8.55
α -Benzoylamino-p-methoxycinnamic acid	$C_{22}H_{25}O_4N_2$	105-109	6.69	6.92

EXPERIMENTAL

I. 2-Phenyl-4-benzylidene-5-oxazolone

40 ml of acetic anhydride was added to a mixture consisting of 26.5 g of freshly-distilled benzaldehyde, 22.5 g of hippuric acid, and 17.25 g of anhydrous potash. After 3-5 minutes, evolution of carbon dioxide began, rapid dissolution of the initial products took place, and the whole solution immediately solidified, the temperature of the reaction mass rising to 120°. On the following day, the crystalline mass was ground with water, filtered, and washed, first with 10% acetic acid, and then with water, to the appearance of a transparent wash water. Air-dried. M.p. 165.5-167° A sample mixed with 2-phenyl-4-benzylidene-5-oxazolone melted without depression. The yield was 26.2 g, i.e., 83.79% of theoretical.

II. 2-Methyl-4-benzylidene-5-oxazolone.

14.75 g of acetic acid, 8.6 g of anhydrous potash, 6.5 g of freshly distilled benzaldehyde, and 40 ml of acetic anhydride were mixed. Temperature of the reaction mass rose spontaneously to 30-32°, and evolution of carbon dioxide began. After 15 minutes, when the temperature began to decrease, the flask was gradually heated (to 60° after 25-30 minutes) and this temperature was maintained for 1 hour; violent evolution of carbon dioxide occurred during this time, with foaming of the entire mass and the separation of a crystalline precipitate. The foaming gradually subsided; the temperature was increased to 120° over a period of 1 hour, and then heated at 120-135° for another hour, whereupon the crystalline precipitate disappeared at 80° and the entire mass converted to a dark liquid which crystallized upon cooling. The crystals on the following day were ground with 75 ml of water and filtered. The precipitate was washed with 10% acetic acid, water, and air-dried. The yield was 20.2 g (85% of the theoretical). M.p. 146-148°.

III. 2-Phenyl-4-(p-methoxybenzylidene)-5-oxazolone

2-Phenyl 4-(p-methoxybenzylidene)-5-oxazolone was synthesized under the same conditions as with 2-phenyl-4-benzylidene-5-oxazolone, the temperature not exceeding 46° when using potash, and the reaction being carried out at 60° when using sodium bicarbonate. The yield of 2-phenyl-4-(p-methoxybenzylidene)-5-oxazolone was 80-85%, m.p. 150-153°.

IV. 2-Phenyl-4-(o-nitrobenzylidene)-5-oxazolone

10 g of hippuric acid, 8.5 g of o-nitrobenzaldehyde, 4.7 g of sodium bicarbonate, and 20 ml of acetic anhydride were heated to 50-55°, and the temperature maintained to cessation of carbon dioxide evolution. Allowed to stand overnight; the following day the reaction mass was mixed with alcohol and filtered. The precipitate was washed with 2% soda solution, dried, and crystallized from acetic acid or alcohol. The yield was 82% M.p. 160-164°.

V. 2-Methyl-4-(o-nitrobenzylidene)-5-oxazolone.

5 g of acetic acid, 6.5 g of o-nitrobenzaldehyde, 3.72 g of sodium bicarbonate, and 9.5 ml of acetic anhydride were heated on a water bath at 55-67° for 2 hours. Allowed to stand overnight. On the following day it was mixed with 10 ml of alcohol and filtered after 1 to 2 hours standing. The residue was crystallized from alcohol. After cooling the alcoholic solution, a mixture of oxazolone and the ester of α -acetylamino-o-nitrocinnamic acid, m.p. 92-98°, precipitated. α -Acetylamino-o-nitrocinnamic acid remained in the alcoholic mother liquor. The mixture with a m.p. of 92-98° was mixed with a small quantity of ether. The undissolved portion was filtered off, and the ether distilled off. The residue represented 2-methyl-4-(o-nitrobenzylidene)-5-oxazolone and was crystallized from benzene. M.p. 110-112°.

Found %: N 12.03. $C_{11}H_9O_4N_2$. Calculated %: N 12.07.

The crystals of α -acetylamino-o-nitrocinnamic acid ethyl ester, which did not dissolve in the ether, were crystallized from benzene. M.p. 121-123°.

Found %: N 9.80. $C_{13}H_{13}O_5N_2$. Calculated %: N 10.03.

α -Acetylamino-o-nitrocinnamic acid. 0.5 g of 2-methyl-4-(o-nitrobenzylidene)-5-oxazolone and 5 ml of a 2% solution of sodium hydroxide were left standing for several hours to the complete dissolution of oxazolone. 15% hydrochloric acid was added to the transparent liquid, to an acid reaction with Congo red. It was filtered, washed with water, and dried. M.p. 201-203°, with decomposition. 0.52 g of α -acetylamino-o-nitrocinnamic acid resulted. The yield was 98%.

Found %: N 10.97; M 254.5. $C_{13}H_{13}O_5N_2$. Calculated %: N 11.19; M 250.08.

The anilide and piperidide of α -acetylamino-o-nitrocinnamic acid. 0.5 g of 2-methyl-4-(o-nitrobenzylidene)-5-oxazolone was dissolved in 10 ml of dry benzene, and 0.3 ml of aniline added to the solution. After several minutes the anilide began to precipitate, and was filtered off after 1-1.5 hours and washed with benzene and ether. It was crystallized from aqueous alcohol. The melting point of α -acetylamino-o-nitrocinnamic acid anilide was 199-201° (with decomposition).

Found %: N 12.58. $C_{17}H_{15}O_4N_3$. Calculated %: N 12.91.

0.5 g of methyl-4-(o-nitrobenzylidene)-5-oxazolone was dissolved in 10 ml of dry benzene, and 0.2 ml of piperidine was added to the solution. The solution became red in color and heat was spontaneously evolved. Benzene was distilled off in vacuo. The residue was ground with ether and filtered. It was recrystallized twice from 50% methyl alcohol. M.p. was 214-216°.

Found %: N 12.96. $C_{16}H_{13}O_4N_3$. Calculated %: N 13.24.

VI. 2-Phenyl-4-isopropylidene-5-oxazolone

10 g of hippuric acid, 4.6 g of sodium bicarbonate, 16 ml of acetic anhydride, and 165 ml of acetone were heated on a water bath at 60-63° for 6 hours. On the following day, the precipitate of sodium benzoate was filtered off; it was obtained in the amount of 23-29% (calculating on the basis of hippuric acid). The filtrate was evaporated in vacuo, and after 100-110 ml of acetone had distilled, the residue, while still warm, was poured into water and allowed to stand overnight. The precipitate was then filtered off, washed with water, 2% solution of soda, again with water, and then dried in the air. 6.6 g resulted, which was recrystallized from 80% alcohol. The yield was 5.6 g, i.e., 50% of the theoretical. The melting point of the 1-phenyl-4-isopropylidene-5-oxazolone was 94-97°. Upon condensing hippuric acid with methylethyl ketone under the conditions of Experiment VI, sodium benzoate was formed in the amount of 20-25%. 2-Phenyl-4-secondary-butylidene-5-oxazolone resulted as a mixture of two geometrical isomers.

VII. 2-Phenyl-4-[1'-(p-nitrophenyl)-ethylidene]-5-oxazolone.

3.26 g of hippuric acid and 1.26 g of anhydrous potash were mixed, and to the mixture was added 5.78 g of acetic anhydride. Reaction started after 2-5 minutes, as evidenced by evolution of carbon dioxide bubbles. When carbon dioxide evolution decreased, 3 g of p-nitroacetophenone was introduced, and the temperature decreased 4-5° at the same time. The reaction mass was heated for 20 minutes at 44°. Gradual dissolution of the precipitate took place, and the entire mass then suddenly crystallized. It was heated up to 49° for some time and then left to stand overnight. On the following day a mixture of ice and water (40 g) was introduced into the flask, and after one hour standing, was filtered. The orange-colored precipitate was washed with water, 4% sodium bicarbonate, again with water, and dried. It was crystallized from alcohol. Oxazolone in the form of yellow crystals with m.p. 175-177° resulted. The yield was 28% of theoretical.

Found %: C 65.92; H 3.84; N 9.12. $C_{17}H_{12}O_4N_2$. Calculated %: C 66.21; H 3.92; N 9.09.

After the technical oxazolone was washed several times with alcohol to separate traces of initial product and the yellow oxazolone crystals, the red crystals of oxazolone were left behind. The melting point of these crystals was the same as for the yellow crystals. The red oxazolone dissolved with heating in alcohol, benzene, and dioxane. It precipitated from the solutions as the yellow crystalline form. The red crystals dissolved in pyridine in the cold, and were precipitated by water from solution as the yellow crystals.

α -Benzoylamino- β -(p-nitrophenyl)-crotonic acid. 0.5 g of 2-phenyl-4-[1-(p-nitrophenyl)-ethylidene]-5-oxazolone was boiled for 5 minutes with 10 ml of a 2% solution of sodium hydroxide. Carbon was added to the turbid solution, filtered, and the solution acidified with hydrochloric acid to Congo red. The colorless crystals were filtered off. The yield was 0.43 g (81% of theoretical). Upon recrystallization from alcohol, the α -benzoylamino- β -(p-nitrophenyl)-crotonic acid melted at 202-204° (with decomposition).

Found %: N 8.58. $C_{17}H_{15}O_5N_2$. Calculated %: N 8.61.

The methyl ester of α -benzoylamino- β -(p-nitrophenyl)-crotonic acid. 0.25 g of oxazolone was dissolved in 25 ml of methyl alcohol, to which traces of sodium alcoholate were added, and left to stand for 24 hours. It was then dissolved in water and the resulting precipitate filtered off. It was crystallized from 80% alcohol. The melting point of the methyl ester of α -benzoylamino- β -(p-nitrophenyl)-crotonic acid was 181-183°.

The anilide of α -benzoylamino- β -(p-nitrophenyl)-crotonic acid. 0.5 g of 2-phenyl-4-[1-(p-nitrophenyl)-ethylidene]-5-oxazolone, 0.2 g of aniline, and 10 ml of dry benzene were boiled for 2 hours. After cooling, it was filtered off; the mother liquor was evaporated in vacuo, the resulting precipitate added to the first and ground with a small quantity of ether. 0.52 g resulted, i.e., 81% of theoretical. The anilide of α -benzoylamino- β -(p-nitrophenyl)-crotonic acid, recrystallized from benzene-acetone mixture (2:1), melted at 251-252° (decomposition).

Found %: C 68.89; H 4.65. $C_{23}H_{19}O_4N_2$. Calculated %: C 68.80; H 4.77.

The piperidide of α -benzoylamino- β -(p-nitrophenyl)-crotonic acid. Upon heating 2-phenyl-4-[1-(p-nitrophenyl)-ethylidene]-5-oxazolone with piperidine, the piperidide of α -benzoylamino- β -(p-nitrophenyl)-crotonic acid resulted, and, after crystallization from dioxane, melted at 211-213° (with decomposition).

Found %: N 10.89. $C_{23}H_{23}O_4N_3$. Calculated %: N 10.67.

VIII. 2-Phenyl-4-[1'-(m-nitrophenyl)-ethylidene]-5-oxazolone.

1.9 ml acetic anhydride was added to a mixture of 1.09 g of hippuric acid and 0.42 g of potash. 1 g of m-nitroacetophenone was then introduced and the temperature gradually brought up to 60° within an hour. It was allowed to stand overnight at room temperature. It was treated as in the preceding experiment. 2-Phenyl-4-[1'-(m-nitrophenyl)-ethylidene]-5-oxazolone was recrystallized from ethyl acetate. M.p. 174-176°. The yield was 0.25 g, i.e., 13.3% of the theoretical.

Found %: N 9.18. $C_{17}H_{15}O_4N_2$. Calculated %: N 9.09.

Upon heating the oxazolone with a 2% solution of sodium hydroxide, α -benzoylamino- β -(m-nitrophenyl)-crotonic acid resulted. It was crystallized from alcohol. M.p. 197-198°, with decomposition.

Found %: N 8.33. $C_{17}H_{15}O_5N_2$. Calculated %: N 8.58.

The piperidide of α -benzoylamino- β -(m-nitrophenyl)-crotonic acid. 0.25 g of 2-phenyl-4-[1'-(m-nitrophenyl)-ethylidene]-5-oxazolone, 0.59 g of piperidine, and 8 ml of dry benzene were boiled for 1 hour. The resulting solution was evaporated in vacuo. The residue was ground with ether and crystallized from alcohol-dioxane mixture (3:1). The melting point of the piperidide of α -benzoylamino- β -(m-nitrophenyl)-crotonic acid was 216-217° (with decomposition).

Found %: N 10.87. $C_{22}H_{23}O_4N_3$. Calculated %: N 10.67.

IX. Quaternary ammonium compounds of saturated and unsaturated amino acids with piperidine.

All of the salts indicated in Table 2 were obtained in the same manner as that described below for the salt of acetyllecine with piperidine. 0.5 g of acetyllecine was mixed with 10 ml of dry benzene, and 0.5 ml of piperidine was added to the resulting suspension. After addition of the piperidine, the precipitate was dissolved, and then a crystalline precipitate began to separate from the solution. The yield was 0.6 g. It was crystallized from a mixture of methyl alcohol and acetone, or was dissolved in methyl alcohol and precipitated with acetone. M.p. 146-147°.

Found %: N 10.51. $C_{19}H_{29}O_3N_2$. Calculated %: N 10.84.

SUMMARY

1. Acetophenone does not react with hippuric acid under conditions of the Erlenmeyer reaction. The nitro group, when introduced into the acetophenone molecule, activates the carbonyl group, and so nitroacetophenone reacts with hippuric acid.

2. 2-Methyl-4-o-nitrobenzylidene-5-oxazolone has been synthesized. It has been demonstrated that the properties of the oxazolone ring differ from those of the oxazolone ring of an unsaturated oxazolone, because this ring is readily split in the cold by alkalies and bases.

3. It has been demonstrated that the use of sodium bicarbonate in the condensation reaction of aldehydes and ketones with acylglycines makes it possible to synthesize oxazolones in the same yields as with potash.

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Received April 15, 1953.

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* See Consultants Bureau Translation, p. 1923.

CYCLOALKYLATION OF AROMATIC COMPOUNDS

VI. CONDENSATION OF 1-METHYLCYCLOPENTANOL AND 1-CHLORO-1-METHYLCYCLOPENTANE

WITH BENZENE

N. G. Sidorova and E. A. Dubnikova

The alkylation of aromatic compounds by methylcyclopentane has received but little study. Condensation of 1-chloro-1-methylcyclopentane with benzene, phenol, and cresol in the presence of ferric chloride [1] has been described, as well as condensation of 1-methylcyclopentanol with phenol in the presence of aluminum chloride [2]. Upon condensing 1-chloro-1-methylcyclopentane with benzene, there were obtained a liquid monoalkylated product, 1-methyl-1-phenylcyclopentane in 37% yield (of theoretical), and a solid disubstituted product. The products were characterized only by their constants. However, there has been observed [3] production of 1-methyl-1-phenylcyclopentane as a result of the abnormal reaction of the acid chloride of 1-methylcyclopentane-1-carboxylic acid with benzene in the presence of aluminum chloride.

The authors studied condensation of 1-methylcyclopentanol with benzene in the presence of aluminum chloride. To avoid a possible isomerization, with expansion of the ring, we carried out the condensation under very mild conditions — in a large excess of benzene (15 moles) and with a very slow addition of aluminum chloride at room temperature. After standing for 24 hours, the reaction mixture was gradually brought to boiling. The monoalkylated hydrocarbon resulted in 43% yield; no definite product separated from the high-boiling fraction. To identify the monoalkylated product by the usual procedure, the nitro compound was obtained, m.p. 58°, which corresponded closely to the melting point for p-nitrocyclohexylbenzene. However, further conversion of the nitro compound into the acetamino derivative gave a substance melting at 141°, as contrasted with a melting point of 130-131° for the acetaminocyclohexylbenzene. This result indicated definitely that the substance obtained by alkylation was 1-methyl-1-phenylcyclopentane. It was characterized by a large number of derivatives.

For an explanation of the existence of cyclic isomerization in this reaction, the condensation was carried out under harsher conditions — with a small benzene excess and rapid AlCl_3 addition, which was accompanied by a boiling up of the reaction mixture. The hydrocarbon resulting from this operation was also found to be mainly the 1-methyl-1-phenylcyclopentane.

An attempt to effect condensation in the presence of phosphoric acid led to a substance of strong aroma, resembling mint, apparently the methylcyclopentane dimer (possibly with an impurity of alkylation product).

In addition, condensation of 1-chloro-1-methylcyclopentane with benzene was carried out by the authors; two hydrocarbons were obtained — 1-methyl-1-phenylcyclopentane (33%) and p-di-(1-methylcyclopentyl)-benzene with m.p. 92°.

The results indicated that under the conditions of these condensations there is no significant isomerization of five-membered rings to six-membered, whereas individual homologs of cyclopentane, according to the data of Turova-Polyak [4], convert to a considerable degree into cyclohexane under the action of aluminum chloride.

EXPERIMENTAL

1-Methylcyclopentanol was obtained from CH_3MgI and cyclopentanone [5]. The yield was 45% of theoretical. B.p. 75° (80 mm); m.p. 35-37°.

1-Chloro-1-methylcyclopentane was obtained by the action of fuming hydrochloric acid upon 1-methylcyclopentanol. After a half-hour shaking with pre-cooled reagents, the mixture was left to stand, the upper layer washed with sodium bicarbonate solution, then with water, dried with calcium chloride, and finally distilled. The yield was 55% of theoretical. B.p. 66-67° (160 mm); n_D^{20} 1.4455.

Condensation of 1-Methylcyclopentanol with Benzene

Condensation I. The reaction was carried out in the usual apparatus without stirrer. 6.5 g (0.05 mole) of aluminum chloride was added in small portions over a period of 2 hours with periodic vigorous shaking to 8 g (0.08 mole) of 1-methylcyclopentanol and 100 ml (1.1 mole) of benzene. Each portion was added only after complete dissolution of the preceding portion; no HCl evolution was observed in this procedure. After completion of the AlCl_3 addition, the mixture was allowed to stand overnight, and was then gradually heated to boiling on a boiling water bath. After cessation of HCl evolution the mixture was cooled and decomposed. After the usual treatment, 5.5 g (43%) was obtained of 1-methyl-1-phenylcyclopentane — a mobile liquid of pleasant odor, resembling that of carrots. B.p. 110–112° (25 mm); d_4^{20} 0.9396; n_D^{20} 1.5193; M_R^D 51.69; calculated 51.82.

Found %: C 89.80; H 9.89. $\text{C}_{12}\text{H}_{16}$. Calculated %: C 90.00; H 10.00.

According to the literature data [1]: 1-methyl-1-phenylcyclopentane has a b.p. of 94–95° (10 mm); d_4^{20} 0.9446; n_D^{20} 1.5241.

p-Nitro-(1-methylcyclopentyl)-benzene. Obtained by treating 3 g of the hydrocarbon with 12 ml of nitrating mixture, at first in the cold, and then with heating on a warm water bath (50–60°). Separation was as usual. The yield was 2.55 g (66%). The b.p. was 130–133° (15 mm). Immediately following distillation, the nitro compound crystallized. The crystals were in the form of yellow needles with m.p. 55°. After three recrystallizations from alcohol, the melting point reached 58°.

5.13 mg substance: 0.350 ml N_2 (27°, 726 mm). Found %: N 7.06. $\text{C}_{12}\text{H}_{15}\text{NO}_2$. Calculated %: N 6.83.

The amine resulted on reduction with tin and hydrochloric acid, and after purification was converted to solid derivatives.

p-Acetamino-(1-methylcyclopentyl)-benzene. M.p. 140–141°. Platelets (from dilute alcohol).

4.31 mg substance: 0.280 ml N_2 (27°, 726 mm). Found %: N 6.73. $\text{C}_{14}\text{H}_{19}\text{NO}$. Calculated %: N 6.45.

p-Benzamino-(1-methylcyclopentyl)-benzene. M.p. 176° (from dilute alcohol). Fine, opaque needles in star clusters.

5.37 mg substance: 0.270 ml N_2 (19°, 731 mm). Found %: N 5.45. $\text{C}_{15}\text{H}_{21}\text{NO}$. Calculated %: N 5.02.

Picrate of p-(1-methylcyclopentyl)-aniline, melted with decomposition at 191–195°. Dark yellow, very fine needles (from benzene and ligroin mixture).

3.91 mg substance: 0.505 ml N_2 (20°, 739 mm). Found %: N 14.13. $\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_7$. Calculated %: N 13.86.

p-(1-Methylcyclopentyl)-benzenesulfonamide [6]. Thick, transparent needles (benzene + ligroin) with m.p. 137–138°.

10.72 mg substance: 0.603 ml N_2 (18.5°, 725 mm). Found %: N 6.05. $\text{C}_{12}\text{H}_{17}\text{NSO}_2$. Calculated %: N 5.86.

p-(1-Methylcyclopentyl)-benzenesulfoanilide. M.p. 118–119°. Transparent prisms (from ligroin).

9.96 mg substance: 0.443 ml N_2 (18°, 729 mm). Found %: N 4.83. $\text{C}_{13}\text{H}_{21}\text{NSO}_2$. Calculated %: N 4.44.

Condensation II. 4.2 g (0.042 mole) of 1-methylcyclopentanol was taken for reaction, plus 15 ml (0.17 mole) of benzene and 3.4 g (0.026 mole) of AlCl_3 . Addition of the AlCl_3 was carried out rapidly and caused violent evolution of HCl. Immediately following addition of all the AlCl_3 , the mixture was boiled for 1 hour. Further treatment was as usual. 1.4 g (21%) of the alkylation product was obtained, consisting mainly of 1-methyl-1-phenylcyclopentane.

B.p. 104–107° (20 mm); n_D^{20} 1.5153; d_4^{20} 0.9296; M_R^D 51.97. Calculated 51.82.

The acetamino derivative melted at 140°. The sample mixed with a sample of the amino derivative of 1-methyl-1-phenylcyclopentane obtained from the preceding reaction did not produce depression in melting point.

Condensation of 1-Chloro-1-methylcyclopentane with Benzene

The reaction was carried out in a two-necked flask with mechanical stirring. 0.5 g (0.004 mole) of aluminum chloride was added in several portions to a mixture of 8 g (0.07 mole) of the chloride and 100 ml (1.1 mole) of benzene cooled to –15°. The reaction mixture was heated on a water bath for 1 hour. After the usual treatment, 3.3 g (33%) of 1-methyl-1-phenylcyclopentane with b.p. 148–150° (100 mm) resulted, along with

0.8 g (10%) of p-di-(1-methylcyclopentyl)-benzene, which distilled at 150-200° (100 mm). M.p. 92° (from dilute alcohol).

According to the literature data: p-di-(1-methylcyclopentyl)-benzene melts at 94° [1].

The constants for 1-methyl-1-phenylcyclopentane were: b.p. 120-122° (30 mm); n_D^{20} 1.5194; d_4^{20} 0.9383; MR_D 51.83; calculated 51.82.

Found %: C 89.76; H 9.90. $C_{12}H_{16}$. Calculated %: C 90.00; H 10.00.

The nitrocompound: m.p. 58°.

SUMMARY

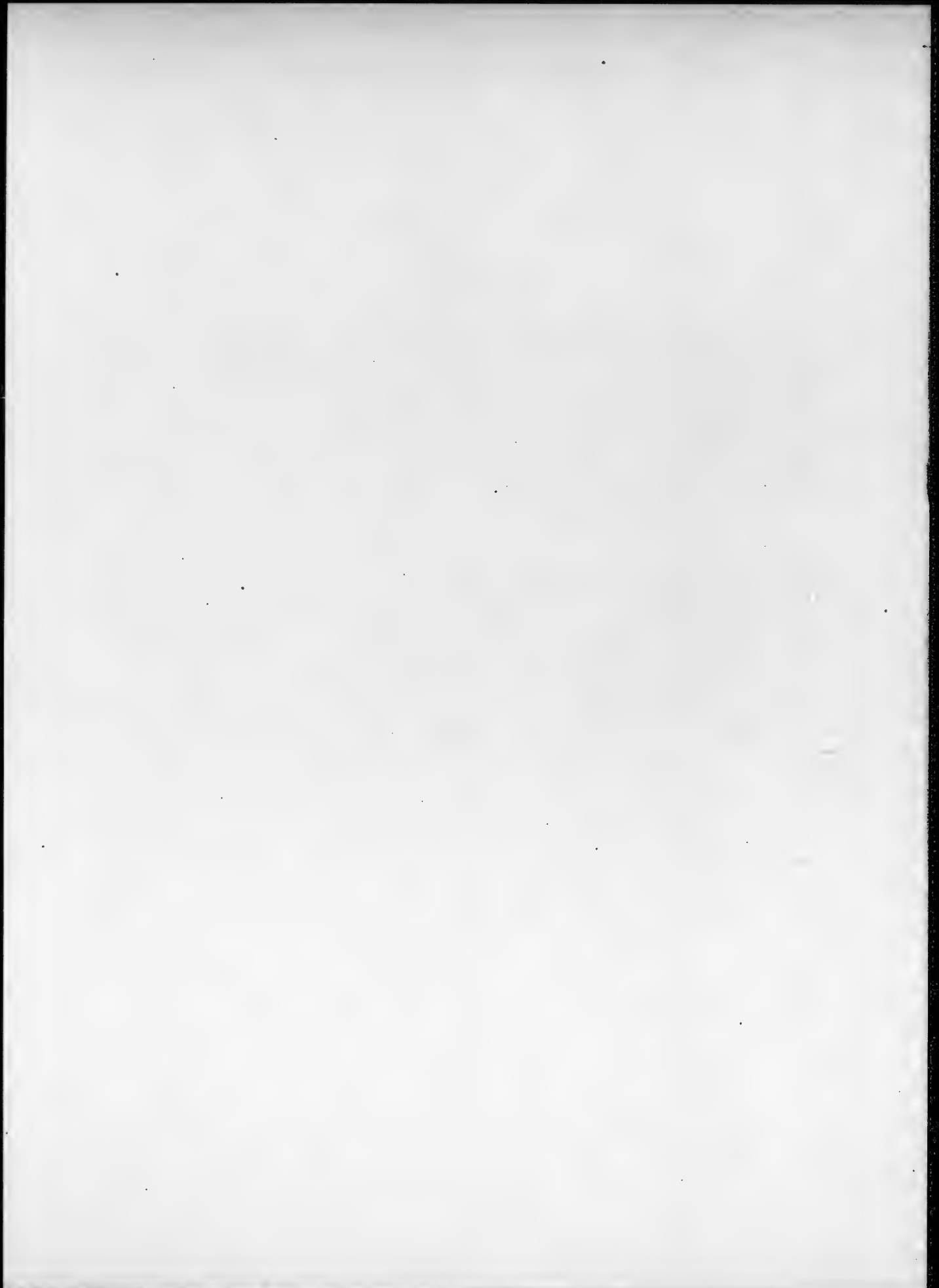
The alkylation of benzene with 1-methylcyclopentanol and 1-methyl-1-chlorocyclopentane has been studied in the presence of aluminum chloride. It has been demonstrated that these reactions proceed without noticeable isomerization, with formation of 1-methyl-1-phenylcyclopentane. A number of crystalline derivatives of 1-methyl-1-phenylcyclopentane have been obtained.

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Received December 15, 1952.

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INTERACTION OF NICOTINE WITH METAL SALTS

II. THE INTERACTION OF NICOTINE WITH THIOCYANATE SALTS

OF NICKEL, IRON (2+), COPPER (2+), MANGANESE, CADMIUM, AND ZINC

S. E. Burkat

In our preceding article [1], results on a study of the reaction between the cobalt thiocyanate complex and nicotine in aqueous solution were given. It was established that the reaction product represented a double salt of nicotine thiocyanate and of cobalt thiocyanate. The conditions of synthesis of this salt were developed, the composition and properties of this compound were studied, and it was demonstrated that it corresponded to the formula: $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Co(CNS)_2$.

In previously published works [2,3], the authors noted that nicotine gives characteristic crystalline precipitates not only with cobalt thiocyanate, but with thiocyanate salts of other metals as well.

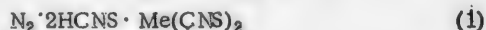
This given investigation was undertaken for the purpose of studying the composition and properties of reaction products between nicotine and nickel, iron (2+), copper (2+), manganese, cadmium, and zinc salts.

Experiments have shown that when nicotine, or its salts, is added to an aqueous solution of one of the above-enumerated metals, in the presence of ammonium thiocyanate, a crystalline precipitate forms, characterized by stability and by constant composition. Such compounds can be obtained with both pure preparations of nicotine and its salts with mineral acids, and with technical nicotine sulfate, or aqueous extracts of tobacco.

The products of interaction of nicotine with thiocyanate salts of the above-indicated metals represent crystalline substances slightly soluble in water, more readily so in hot water. They crystallize readily from water. The compounds obtained dissolve in dilute mineral acids, and again separate out from solution after neutralization with alkali. They dissolve in concentrated sulfuric and hydrochloric acids without any characteristic peculiarities. With the aid of standard reagents, the presence of the corresponding metal ions, thiocyanate ions and nicotine in saturated aqueous solutions of the compounds obtained by qualitative procedures is readily established. Aqueous solutions of these compounds are titrated with alkali, which indicates the presence of nicotine in their composition,

in the form of a salt. The characteristics shown by the compounds obtained give grounds for considering them to be binary salts of nicotine thiocyanate, and thiocyanates of the above-cited metals. Analysis of the substances obtained has indicated that their composition can be represented by formulas (1) and (2):

No.	Formula	Melting point*
1	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Ni(CNS)_2$	237-238°
2	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Fe(CNS)_2$	200-201
3	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cu(CNS)_2$	135-136
4	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Mn(CNS)_2$	207-208
5	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cd(CNS)_2$	209-210
6	$C_{10}H_{14}N_2 \cdot HCNS \cdot Zn(CNS)_2$	180-181



where N = an integer number for nicotine, Me = metal.

The compounds obtained are given in the table.

* The compounds melt with partial decomposition

EXPERIMENTAL

1. Synthesis of Nicotine Thiocyanate and Nickel Thiocyanate Binary Salt

2.9 g of crystalline nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 5 ml of water. A solution of 3.1 g of ammonium thiocyanate in 5 ml of water was prepared in a separate container, and the two solutions were mixed. 3.25 g of nicotine (base) was placed in a 100 ml flask, 20 ml of water added, and the resulting solution neutralized with 25% hydrochloric acid solution (indicator — methyl red). A solution of the nickel thiocyanate complex was added to the prepared nicotine solution, with vigorous stirring, and the mixture left for 15 minutes. The resulting precipitate was filtered off with suction, washed with 5-10 ml of water on the filter, and dried at 60°. The yield

of resulting precipitate was 90% of theory, assuming that the reaction proceeded according to the following equation:



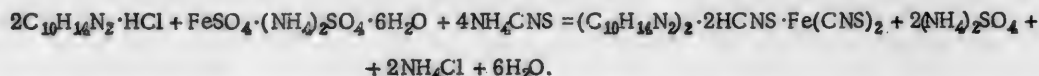
The resultant product was twice recrystallized from boiling water (the first time from 120 ml, and the second time from 100 ml). The crystalline powder was blue in color and without odor. The solubility in water at 20° was 0.60%. An aqueous solution was faint blue in color.

Quantitative determination of the metal, the thiocyanate ion and the nicotine was carried out according to standard analytical procedures.

0.3010, 0.3000, 0.4040 g substance. Found %: Ni 9.64, 9.16, 9.24; CNS' 36.61, 35.60, 35.15; nicotine 51.33, 51.78, 51.52. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Ni(CNS)_2$. Calculated %: Ni 9.50; CNS' 37.50; nicotine 52.47.

2. Synthesis of Nicotine Thiocyanate and Iron Thiocyanate Binary Salt

3.9 g of Mohr's salt and 3.1 g of ammonium thiocyanate were dissolved separately in 5 ml of water and the solutions were then mixed. 3.25 g of nicotine (base) was dissolved in a separate container, the resultant liquid neutralized with hydrochloric acid, and the above-prepared iron thiocyanate complex added with vigorous stirring. The resulting crystalline precipitate was filtered with suction, washed on the filter with 5 ml of cold water, and dried at 60°. The yield of substance was 80%, calculating for the nicotine taken in reaction.



The resultant compound was recrystallized twice from boiling water (the first time from 50 ml of water, and the second time from 40 ml) and dried between sheets of filter paper at room temperature.

Lustrous crystals, light-brown in color. Solubility in water at 20°—1.95%. The aqueous solution was yellow in color.

0.5000, 0.3000, 0.5030 g substance: Found %: Fe 9.48, 9.80, 9.25; CNS' 35.80, 36.00, 36.45; nicotine 52.92, 53.14, 53.00. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Fe(CNS)_2$. Calculated %: Fe 9.10; CNS' 37.79; nicotine 52.76.

3. Synthesis of Nicotine Thiocyanate and Copper Thiocyanate Binary Salt

5 g of crystalline copper sulfate $CuSO_4 \cdot 5H_2O$ was dissolved in 20 ml of water, and 10 g of crystalline ammonium thiocyanate was added to the resultant solution. The solution was filtered. 3.25 g of nicotine (base) premixed with 20 ml of water and neutralized with 25% hydrochloric acid, was added with vigorous stirring to 10 ml of the filtrate. The resulting precipitate was filtered by suction, washed on the filter with 5-10 ml of water, and dried between sheets of filter paper at room temperature. The yield of resultant product was 75%, calculating on the basis of nicotine taken for reaction.



Fine powder, green in color. The resultant salt was not very soluble in cold water. It decomposed partially on boiling with water, forming a precipitate of copper thiocyanate. Crystals did not separate from the supersaturated aqueous solution. The aqueous solution was green in color.

0.5000, 0.5032, 0.3000 g substance. Found %: Cu 10.16, 10.52, 10.91. Nicotine 51.30, 52.59, 52.42. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cu(CNS)_2$. Calculated %: Cu 10.23; nicotine 52.12.

4. Synthesis of Nicotine Thiocyanate and Manganese Thiocyanate Binary Salt

1.9 g of crystalline manganese thiocyanate $MnSO_4 \cdot 2H_2O$ and 3.1 g of ammonium thiocyanate were dissolved separately in 5 ml of water, and the two solutions combined. 3.25 g of nicotine (base) was mixed in a separate container with 10 ml of water and the resultant mixture neutralized with 25% hydrochloric acid. Manganese thiocyanate was added to the prepared nicotine solution with vigorous stirring, and the mixture left for 30 minutes. The crystalline precipitate was filtered off by suction and dried at 60°. The yield of compound was 84%, calculating on the basis of nicotine taken for reaction:



The resultant compound was recrystallized twice from boiling water (the first time from 20 ml of water, the second time from 10 ml), and the crystals were dried between sheets of filter paper at room temperature.

A crystalline powder, light-yellow in color. Solubility in water at 20° - 4.4%. The aqueous solution was almost colorless.

0.5000, 0.3000, 0.4998 g substance. Found %: Mn 8.26, 8.13, 8.46; CNS' 35.50, 36.16, 36.54; nicotine 52.30, 52.69, 52.48. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Mn(CNS)_2$. Calculated %: Mn 8.96; CNS' 37.80; nicotine 53.01.

5. Synthesis of Nicotine Thiocyanate and Cadmium Thiocyanate Binary Salt.

1.84 g of anhydrous cadmium chloride, and 3.1 g of ammonium thiocyanate were separately dissolved in 5 ml of water and the solutions mixed. The resulting solution was poured, with vigorous stirring, into 3.25 g of nicotine (base) in 10 ml of water, neutralized beforehand with 25% hydrochloric acid. A light-yellow crystalline precipitate separated. The mixture was allowed to stand for 30 minutes, and the crystalline mass then filtered off by suction and dried at a temperature of 60°. The resultant compound was 86% of theoretical, assuming that formation of the compound occurred according to the following equation:



The resultant compound was recrystallized twice from boiling water (the first time from 100 ml of water, and the second time from 70 ml), and the crystals were dried between filter paper sheets at room temperature.

A white crystalline powder with yellow shade. Solubility in water at 20° - 0.80%. The aqueous solution was colorless.

0.5000, 0.3000, 0.5018 g substance. Found %: Cd 17.20, 16.46, 16.24; CNS' 32.98, 32.76, 33.12; nicotine 48.30, 48.44, 48.39. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cd(CNS)_2$. Calculated %: Cd 16.76; CNS' 34.60; nicotine 48.32.

6. Synthesis of Nicotine Thiocyanate and Zinc Thiocyanate Binary Salt

2.9 g of crystalline zinc sulfate $ZnSO_4 \cdot 7H_2O$ was dissolved in 5 ml of water. A solution of 3.1 g of ammonium thiocyanate in 5 ml of water was prepared in a separate container and the two solutions combined. 3.25 g of nicotine (base) was mixed in a porcelain cup with 10 ml of water and neutralized with 25% hydrochloric acid; the prepared complex solution of zinc thiocyanate was added with stirring to the neutralized nicotine solution. A thick, milky-white turbidity formed, from which there separated out a resinous mass, yellow in color. The liquid was poured off as thoroughly as possible and the resultant mass washed with 10 ml of cold water, and then dissolved in 120 ml of water by boiling, and the solution filtered immediately. Upon cooling, there separated out from the filtrate colorless silky needles. The resultant crystalline mass was repeatedly recrystallized from 80 ml of boiling water, and the crystals dried between filter paper sheets at room temperature. The yield of pure product was 45%, calculating on the basis of nicotine taken for reaction.



Light, feathery, crystalline mass, white in color, with silky sheen. Solubility in water at 20° - 0.80%. The aqueous solution was colorless.

0.5000, 0.5014, 0.3000 g substance. Found %: Zn 16.46, 16.43, 16.25; CNS' 40.00, 41.28, 41.42; nicotine 41.00, 41.14, 41.48. $C_{10}H_{14}N_2 \cdot HCNS \cdot Zn(CNS)_2$. Calculated %: Zn 16.22; CNS' 43.24; nicotine 41.00.

SUMMARY

Binary salts between nicotine thiocyanate and the thiocyanates of nickel, iron (2+), copper (2+), manganese, cadmium, and zinc have been synthesized. The composition, properties, and formulas of the compounds obtained are given in the text of the article.

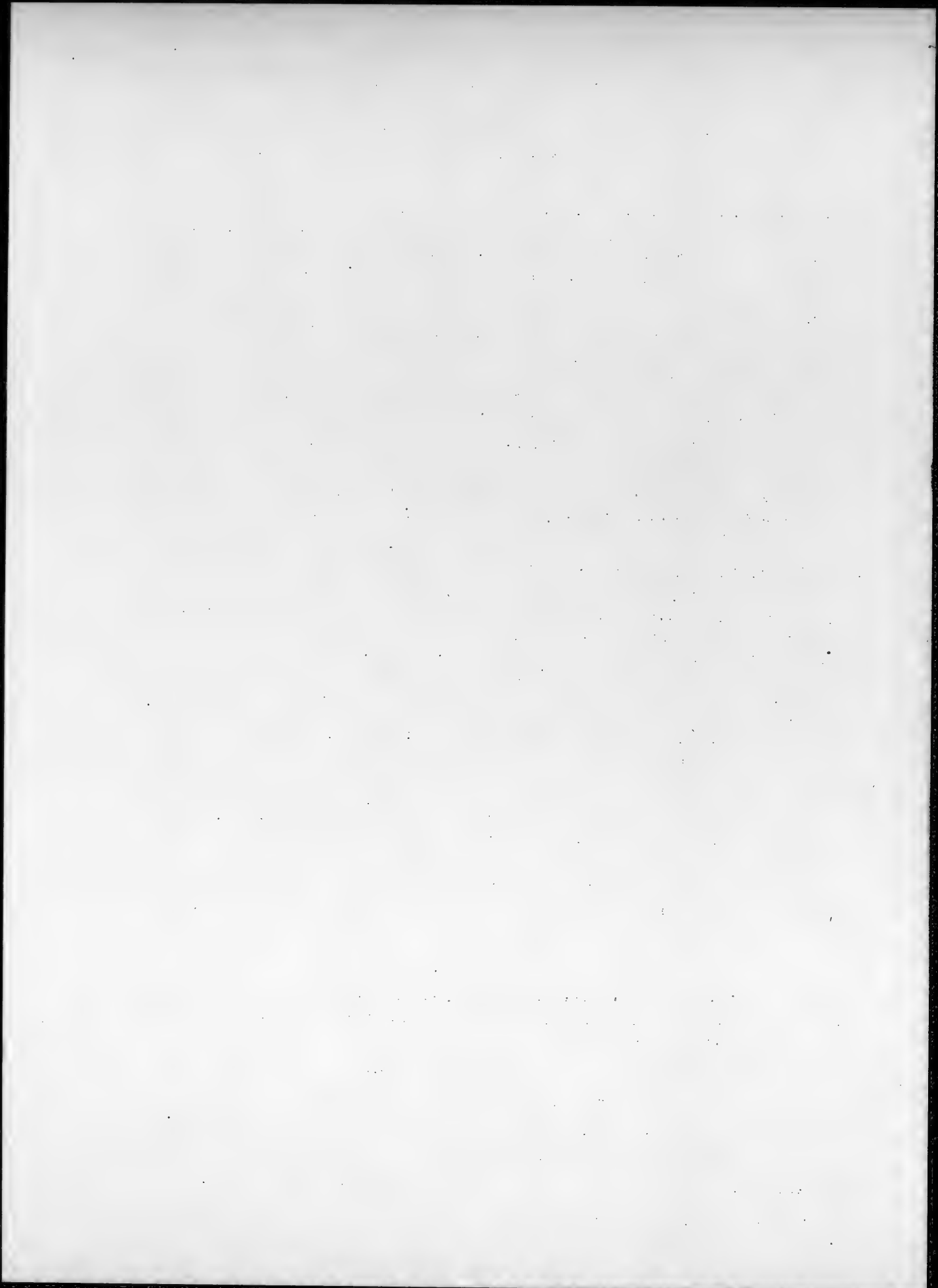
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Received March 22, 1953

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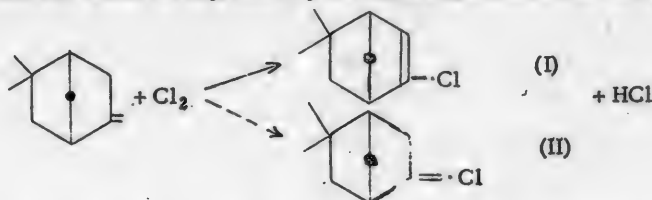


NEW TYPES OF TERPENE TRANSFORMATIONS

XV. THE ACTION OF CHLORINE UPON β -FENCHENE

D. Tishchenko and S. Sheina

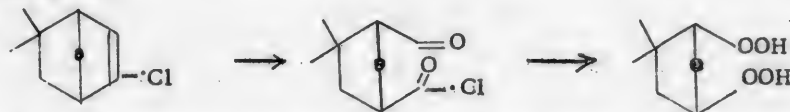
In article I [1], the authors developed a general concept for predicting the structures of unsaturated chloro-terpenes which should be formed by the interaction of chlorine with any terpene. Additional ideas on the subject were given in subsequent articles XI and XIV [2]. In accordance with these, it could be foreseen that the interaction of chlorine with β -fenchene would be expressed by the following scheme (the saturated dichloride is not presented):



The possibility of forming the chloride (II) is explained by the same causes as for the corresponding chlorides of camphene and α -fenchene [2]. The reaction of chlorine with β -fenchene has not been studied by anyone, and the accuracy of our assumptions could only be verified experimentally.

β -Fenchene was synthesized according to the method of Qvist [3], by dehydrating fenchilic alcohol with potassium acid sulfate, and separated from the accompanying γ -fenchene by fractionation on an efficient column. Its constants corresponded to the literature data.

Chlorination of β -fenchene was carried out under conditions described many times. By distilling the reaction products, monochloroterpene was isolated, boiling within a narrow range, which indicated the absence of isomeric chlorides with various (primary, secondary, and tertiary) position of the chlorine atom. Not all the chlorine (16.9% out of the 20.4%) was found to be mobile, and the molecular refraction of the monochloroterpene exceeded that calculated for chloride (I) by 0.3, which should be attributed to the presence of about one-fourth chloride (II) in the chloroterpene. Upon ozonizing the chloroterpene, chloroketoaldehyde resulted, which upon further oxidation, gave cis-apo-fenchocamphoric acid, which ensured the structure (I) as the principal constituent of the chloroterpene:



Thus, it can be considered that the authors' predictions regarding the interaction mechanism of chlorine with β -fenchene are confirmed by experimental data, and that this mechanism does not differ from that for other terpenes.

EXPERIMENTAL

Synthesis of fenchilic alcohol has been described by the authors [2]. Its dehydration was carried out under the conditions of Qvist [3]. The mixture of fenchenes was fractionated on a column with an efficiency of about 40 theoretical plates, with 15-16 phlegm number, in order to obtain sharply boiling fractions (pressure 10 mm), for which purpose three distillations were necessary. γ -Fenchene was isolated in a yield of 39%, β -fenchene in yield of 34% of the charge. Constants for the β -fenchene: b.p. 43° (at 10 mm); d_4^{20} 0.8654; n_D^{20} 1.4692; MR_D 43.90. Calculated for β -fenchene, 43.91.

Chlorination of β -Fenchene

50 g of fenchene, 30 g of NaHCO_3 , 12.5 g of KMnO_4 , and 70 ml of HCl (sp. gr. 1.17). Cl_2 found in the salts and in the trap was 5.15 g, chlorine in the organic portion was 7.6 g, the percentage abnormal reaction being 80. The reaction product was fractionated on a column of 6-7 plates, at a phlegm number of 15-16 and at a pressure of 8 mm. 17 g of monochloroterpene resulted, with the constants: b.p. 40-42°; d_4^{20} 1.0128; n_D^{20} 1.49165; % Cl 20.4; % allyl chlorine 16.9.

Ozonization of Chloroterpene

5 g of chloroterpene in 5 ml of chloroform was ozonized with ice-cooling (44 liters of 2.4% ozone being consumed), to a negative reaction to bromine. The ozonide solution was stirred with water for 6 hours, the chloroform layer separated, and the chloroform removed from it, weight of the residue being 6.1 g. About 6.0 g of the chloroketoaldehyde may have resulted. The residue was distilled under a pressure of about 1.10^{-3} mm. Most of the fraction distilled off at a bath temperature of about 180°. For it was found: d_4^{20} 1.129; n_D^{20} 1.4902.

Found %: C 59.1, H 7.8. $\text{C}_{10}\text{H}_{15}\text{O}_2\text{Cl}$. Calculated %: C 59.2, H 7.5.

Oxidation of Chloroketoaldehyde

4% permanganate solution was added to 2.4 g of the substance in 50 ml of acetone, and 30 ml of water, to a stable pink coloration (140 ml). The manganese dioxide was extracted three times with boiling water, the combined filtrates evaporated to 50 ml, acidified with sulfuric acid (to Congo), and extracted repeatedly with ether. Ether was removed from the extract, and the residue almost completely solidified to a mush of needle crystals saturated with a viscous liquid. The crystals were filtered off by suction and recrystallized from aqueous alcohol to a constant m.p. of 142-143°.

The equivalent weight of the crystals was found to be 93.9; the silver content of the silver salt was found to be 54.2%. The equivalent weight for cis-apo-fenchocamphoric acid $\text{C}_9\text{H}_{14}\text{O}_4$ is 93.0, and the percent silver of the silver salt 54.0. Nametkin and Khukhrikova have found a m.p. of 144-145° for this acid [4].

SUMMARY

The reaction of chlorine with β -fenchene has been investigated. The principal product has been found to be the chloro- γ -fenchene (I), and a side-product, apparently ω -chloro- β -fenchene (II), which is in agreement with the reaction mechanism of chlorine with terpenes proposed earlier by the authors.

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Received February 12, 1953.

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* See Consultants Bureau Translation, p. 593.

** See Consultants Bureau Translation, p. 1863.

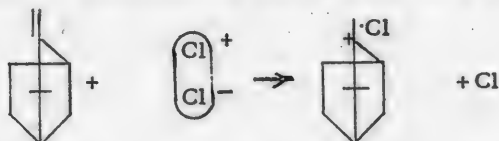
*** See Consultants Bureau Translation, p. 1051.

NEW TYPES OF TERPENE TRANSFORMATIONS

XVI. THE STRUCTURE AND CERTAIN TRANSFORMATIONS OF CAMPHENE DICHLORIDE

D. Tishchenko and I. Uvarov*

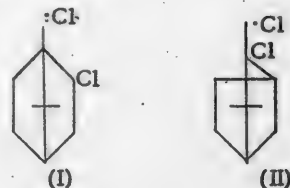
In one of the preceding articles are given the results of a study of the interaction between chlorine and camphene, and the structures of the resulting monochloroterpenes were established at that time [1]. Up to the present time the authors have not investigated the structures of terpenes of the saturated dichlorides, products of the "classical" reaction which result upon chlorination. However, this process is not inactive. From both the scanty experimental data to be had in the literature on this subject, and the more extensive information on the interaction of terpenes with polar or polarizing substances at the time of reaction, do not make allowance for a consideration that addition of two chlorine atoms to a terpene molecule will proceed in any number of cases in accordance with a "principle of least change in structure", nor that the terpene double bond will be saturated with chlorine without a change in the basic structure. Thus Aschan indicated [2] that α -pinene dichloride has the structure of 2,6-dichlorocamphane (conversion of the pinane nucleus to the camphane nucleus). With the analogous retropinacolinic acid, rearrangement proceeds with addition of organic acids to camphene to form esters of isoborneol possessing the camphane nucleus. In a similar fashion, proceeds the addition of hydrogen halide to α - and β -pinenes. At the same time, the action of non-polar reagents, for example of ozone and hydrogen, does not lead to resynthesis of the terpene nucleus. The organic acids and hydrogen halides are without doubt polar reagents. The chlorine atom is formally non-polar, but the authors, and other investigators (see preceding articles) have accepted the fact that it polarizes during reaction. The first product of reaction should be the carbonium cation, capable of undergoing isomeric transformations, which, in the case of camphene, can be represented by the equation:



The chlorine anion can pull off one or more protons [1], or add to the cation, before or after its isomerization. If based upon the analogy of organic acid addition to camphene, then the camphene dichloride should be in the form of 2,10-dichlorocamphane (I) (retropinacolinic regrouping), and not the "normal" camphene dichloride (II).

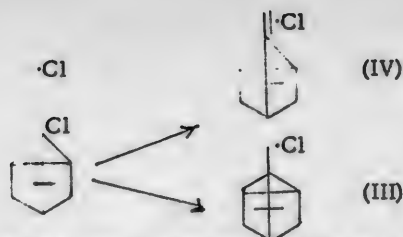
A solution of this reaction process is possible only through the experimental procedure.

Interaction of camphene dichloride with a large excess of sodium in ether solution, followed by subsequent decomposition of the reaction product with aqueous alcohol, gave a mixture of hydrocarbons with a predominance of camphane, containing in addition a new tricyclene (m.p. 110-111°) and some bornylene.

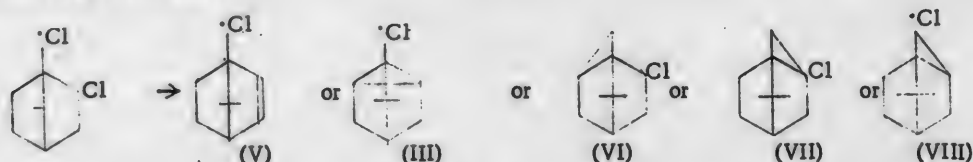


Synthesis of camphane and of bornylene indicated that camphene dichloride has the nucleus of camphane, and not of isocamphane, and that structure (I) is more probable for the dichloride. A study of the dichloride interaction with sodium in moist ether also led to the same results. The removal of one molecule of hydrogen chloride from camphene dichloride of structure (II) can give either the chloride of tricyclene (III) or ω -chloro-camphene (IV):

* The experimental work was carried out by I. Uvarov, member of the students scientific society at the Department of Organic Chemistry, Academy of Wood Technology.

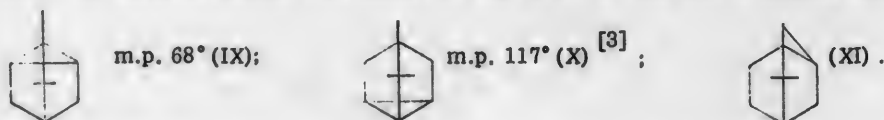


The dichloride (I) will give either chlorobornylene (V), or chlorotricyclene (III), or the chloride of neotricyclene (VI), (VII) and (VIII).



Camphene dichloride does not react in a boiling solution of potassium hydroxide in ethanol, nor does it react with the solution in butyl alcohol if azeotropic removal of the evolving water is assured. A mixture of monochloroterpenes is formed in good yield, consisting of not less than 90% of crystalline chloroterpenes, with m.p. 23-24°, non-oxidizable by potassium permanganate and non-ozonizable by addition to the unsaturated chloroterpene. The monochlorides (III) and (IV) are liquids and are therefore excluded; also excluded is the chloride (V) (which should oxidize and ozonize); formulas of the structures (VI), (VII), and (VIII) are left for investigation. The melting point of this crystalline chloroterpene does not coincide with any of the known chloroterpenes.

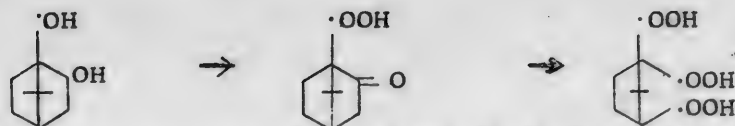
This crystalline chlorotricyclene reacts readily in ether solution with magnesium, with activated ethyl bromide, and gives the corresponding organomagnesium compound in yield not less than 70%. Upon decomposing the organomagnesium compound with water, a crystalline terpene resulted with m.p. 110-111°, non-oxidizable with water and acetone solutions of permanganate, and differing from bornylene in having a sharp melting point at 112-113°. In admixture with bornylene, it melted without depression, but this phenomenon is observed in a number of cases with terpene chemistry. From its non-oxidizability with permanganate, this terpene should be some kind of tricyclene. The known crystalline tricyclenes (IX) and (X) differ from ours in melting points:



The formula for structure (XI) is probable, but the possibility for structure (X) is not excluded. Upon hydration according to the method of Konovalov-Bertran-Walbaum, terpene (X) should produce epiborneol, with m.p. 186°, and terpene (XI) can give either the neoborneol of Akhmatovich with m.p. 186° [4], or borneol with m.p. 202°, or isoborneol with m.p. 212°, or 10-hydroxycamphane.

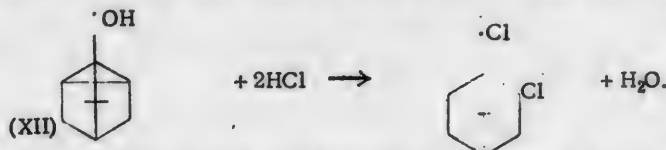
In actuality, the alcohol with a m.p. of 186° resulted. Neoborneol of Akhmatovich gives camphor with m.p. 176° upon oxidation, and epiborneol gives epicamphor with m.p. 180°. Hence, both of these alcohols and their ketone derivatives are indistinguishable from each other. The oxime of camphor melts at 117°, the α -bromocamphor at 76°; the corresponding derivatives of epicamphor melted at 94 and 133°. The oxime of our camphor melted at 117°, and the bromoderivative at 74-76°; hence, our alcohol was found to be neoborneol, and our terpene has the structure of neotricyclene (XI). Synthesis of neotricyclene (XI) from camphene dichloride indicated that chlorine is located in position 2 or 10 in the latter compound; the positions of the other chlorine atoms removed by hydrogen exchange upon decomposition of the organomagnesium compound with water remain unknown.

Oxidation of the organomagnesium compound by oxygen gives a terpene alcohol $C_{10}H_{18}O$ with m.p. 158-160° differing in melting point from that of any known terpene alcohol. This was a secondary alcohol, since it could be oxidized to the corresponding ketone, with a m.p. of about 143°, and since it did not react with phthalic anhydride in boiling benzene, but reacted in boiling xylene to form the phthalate, melting at 104-105° (phenylurethane with m.p. 94-95°); consequently structure (VII) is eliminated. The semicarbazone of the ketone melted at 208-209°, and was distinguished by its melting point from the semicarbazones of ketones $C_{10}H_{16}O$. Upon hydrogenation, the authors' new alcohol gave the corresponding diol $C_{10}H_{18}O_2$, which could be oxidized to the ketopinic and carboxyapocamphoric acids, which is feasible only for the structure 2,10-dihydroxycamphane:



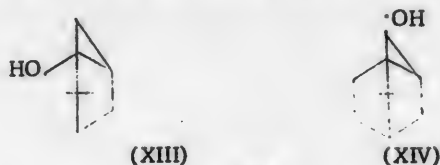
This 2,10-dihydroxycamphane melted at 172-178°, and was distinguished by its melting point from the known dihydroxycamphanes (2,6- 240-242°, 2,5- 233-234°, 2,3- 230-231°). By the same fact, the camphene dichloride possessed the structure (I), of 2,10-dichlorocamphane.

There is described in the literature a dichloride accepted for 2,10-dichlorocamphane, the Komppa dichloride with a m.p. of 58°, obtained by the action of hydrogen chloride upon triclycene (XII) [5]:



This dichloride by the synthetic method could have the structure (I), and in such case should be the stereoisomer of our camphene dichloride. Of course, a final solution to the problem of the structure of the Komppa dichloride can only be found from the experimental approach, perhaps even by the conversions developed by the authors.

The neotricyclenol obtained by the authors, with m.p. 158-160°, may have the structure (XIII) or (XIV):



Its structure was not proved by the authors, due to a lack of time, but it can be proved by oxidation of the alcohol; upon oxidation with permanganate, the alcohol (XIII) should give a dicarboxylic acid, the alcohol (XIV) should give a ketopinic acid, and from it the carboxyapocamphoric acid.

EXPERIMENTAL

Synthesis of camphene dichloride was described earlier [1]. After two or three recrystallizations from methanol or ethanol, a m.p. of 133-134° was obtained, which remained constant after subsequent recrystallizations.

Found %: Cl 34.4, 34.4. $C_{10}H_{16}Cl_2$. Calculated %: Cl 34.3.

Synthesis of Chloroneotricyclene

675 g of dichloride was heated to boiling with a solution of 280 g of potassium hydroxide in one liter of butanol. The reflux condenser was connected with the reaction flask through a water trap. 55 ml of water had separated after 20 hours. The flask contents were mixed with 1 liter of water, the oily layer removed, washed with weak hydrochloric acid, dried with potash, and fractionated on a column with 7-8 theoretical plates of phlegm number 8-10 at 8 mm pressure. After distilling off the butanol, there resulted 266 g of fraction with b.p. 77-79° (the monochloride), 52 g of an intermediate fraction, 79-90°, and 250 g of camphene dichloride. The latter was treated for a second time with potassium hydroxide in butanol. After a final fractionation, 431 g of monochloride resulted with m.p. 77-79° at 8 mm.

Standard bromine solution was added to weighed portions of the monochloride in the amounts of 0.5193 and 0.4368 g, dissolved in chloroform and cooled with snow, to a permanent color; the amount of bromine used was 0.03290 g and 0.0278 g, respectively, which corresponded to a content of about 7% monochloride, with double bond, in the fraction.

50 g of the monochloride fraction was ozonized in carbon tetrachloride with 5% ozone passed through, calculated on the basis of one double bond in the monochloride. After decomposition of the ozonide solution with water, and fractionation of the reaction products, it was found that at least 70% of the initial monochloride failed to react with the ozone. Analysis of the monochloride gave:

d_4^{12} 1.035; n_D^{12} 1.4884; MR_C 47.29; $C_{10}H_{15}Cl$. Calculated 47.12.

0.2010 g substance: 0.1655 g AgCl. 0.2353 g substance: 0.1941 g AgCl. Found %: Cl 20.6, 20.8. $C_{10}H_{15}Cl$. Calculated %: Cl 20.7.

Upon cooling to +11°, the fraction began to crystallize. It was cooled to -8° and filtered with vacuum at the same temperature. 188 g of solid chloride resulted, and 240 g of liquid chloride. The solid chloride was pressed off at room temperature, after which it melted at 24-25°, with a camphor aroma, quite volatile. Its chloroform solution did not decolorize bromine solution; a solution of the liquid portion, however, decolorized. The liquid portion was fractionated repeatedly on the same column at 8 mm with a phlegm number of 15-16. 15 g of fraction was collected with a b.p. of 31-77°, the main fraction being 77-79°, solidifying at -8°. 132 g of the solid chloride was removed and 77 g of the liquid portion which solidified partially at -23°. 320 g of solid chloride resulted, melting at +20°.

Oxidation of solid and liquid monochlorides. Weighed portions of 0.1464 g and 0.2894 g, respectively, were dissolved in acetone, to which was added 1% acetone solution of potassium permanganate. In the first case, 0.2 ml was added over a period of 52 minutes to a stable color, and in the second case, 2.2 ml over a period of 120 minutes. Hence, about 2% chloride with one double bond was present in the solid chloride, and in the second, about 13%.

Purification of the liquid chloride by oxidation. A solution of 7 g of permanganate in acetone was added to 77 g of chloride in 100 ml of acetone. After the usual treatment, 65 g of fraction with b.p. 77-78° at 8 mm resulted, which solidified completely at -8°. After pressing out on paper, m.p. 23-24°.

Synthesis of Camphane and Bornylene from Camphene Dichloride

10 g of sodium in a thin ribbon was put into 400 ml of dry ether, and 20 g of the dichloride added slowly through a reflux condenser. The flask was heated to the boiling point of ether for 20 hours, and the alcohol was then added slowly to dissolution of sodium excess, and the flask contents distilled with steam. The ether layer of the distillate was separated, dried with calcium chloride, and fractionated. The fraction with b.p. 145-160° solidified completely in the cooler, its m.p. 110-114°, and did not contain chlorine. Half of the fraction (3.7 g) was recrystallized three times from alcohol to a m.p. of 151-154°, the fourth crystallization not changing the melting point. The second half was heated with 20 ml of sulfuric acid at 100°. The crystals which sublimed into the reflux condenser (1.5 g) had a m.p. of 148-150° (in a sealed capillary), and after two recrystallizations from alcohol, an unchanging m.p. of 153.5-154°.

0.1150 g substance: 0.3666 g CO₂; 0.1356 g H₂O. Found %: C 86.9; H 13.1. C₁₀H₁₈. Calculated %: C 87; H 13.

A hydrocarbon was isolated from the alcoholic mother liquors, which melted from 100 to 113°. 1.85 g of hydrocarbon in 5 ml of benzene was heated to boiling in a flask with reflux condenser with a solution of 5.7 g of permanganate in 570 ml of water for 16 hours, after which the large unreacted excess permanganate was decomposed with hydrogen peroxide, the manganese dioxide removed with suction, the alkaline solution evaporated to 20 ml, and acidified (to Congo), followed by extraction with ether. Ether was removed from the extract, the small crystalline residue was recrystallized from hot water. 0.3 g of needle crystals resulted, with m.p. 200-201°, and the gram-equivalent of 100.1 corresponded to camphoric acid.

Proof of the presence of neotricyclene in the products of interaction of camphene dichloride with sodium.

94 g of camphene dichloride was dissolved in 400 ml of dry ether, and 22 g of sodium in thin strips was gradually introduced into the solution. After 23 hours, all of the sodium had reacted. 400 ml of water was introduced into the flask, the ether layer removed, dried, and fractionated. The fraction with b.p. 145-170° solidified in the cooler (22.6 g). It was rolled over paper to evaporate the readily-volatile camphane, the weight of the residue being 12.1 g, which was oxidized in an acetone solution of 2.5 g of permanganate, after which procedure the acetone was distilled off, and from the distillate the hydrocarbon which distilled off with the acetone precipitated (8.0 g, m.p. 90-98°). These 8 grams were dissolved, with heating, in 15 ml of alcohol, and upon cooling, 5 g of feathery crystals precipitated, which melted, after prolonged drying over potassium hydroxide, at 104-106°. On hydrogenation of these crystals (see below), neoborneol resulted, with m.p. 186-187° (m.p. of the phenylurethane was 139-140°).

The Interaction of Chlorotricyclene (m.p. 23-24°) with Magnesium.

80 g of magnesium shavings was placed in a flask, equipped as usual, and covered with ether, after which 20 g of chloride was introduced, an iodine crystal, and 1 g of ethyl bromide; after start of the reaction, a solution of 20 g of ethyl bromide and 300 g of the chloride in 500 g of dry ether was added over a period of 5 hours, with stirring and water cooling, after which mixing was continued for another 5 hours. From an aliquot portion of the solution titrated, 1.33 g-equiv. of organomagnesium compound was found, the yield being 71%. The solution was decanted off from the excess magnesium, the magnesium washed with ether, and the solution combined, to a total volume of 1250 ml.

500 ml of this solution was dissolved in water, the ether layer separated, and the ether removed from it, the weight of residue being 87 g. The ether was distilled, the residue dried with powdered potassium hydroxide, and distilled in a fractionating column. From the residue there was obtained 4.5 g of neotricyclene, with m.p. 108-110°. It was volatile with vapors of moist ether.

87 g of residue was fractionated. There was obtained: to 146° 3.3 g; 146-148.5° (160°) 41.8 g; 160-235° 11.2 g; residue 29.8 g. 4.5 g of neotricyclene (see above) was added to the main fraction and 33.3 g (see below) and 79.6 g were fractionated. Result: I) 146-147.5°, 12.2 g, b.p. 108-112°; II) 147.5-148.5° 38.1 g, b.p. 108-111°; III) 148.5-160°, 10.2 g, m.p. 85-103°; IV) 160-235° 11.2 g; residue 18.4 g. Fraction II distilled almost completely at 148.5° upon the second distillation. With the same fractionating set-up and thermometer, known bornylene (m.p. 104-106°) distilled at 146°. 15.7 g of Fraction II did not dissolve in 40 ml of alcohol in the cold, but dissolved upon boiling. After cooling, 8 g of feathery crystals precipitated, m.p. 110-112°, after drying over alkali. Several drops of water was added to the heated mother liquor, the crystals (2.7 g) which precipitated in the cold, melting, after drying, at 110-112°, and the subsequent crystals (3.1 g) also at 110-112°, the last precipitate (0.7 g) at 96-102°.

0.1311 g substance: 0.4254 g CO₂; 0.1404 g H₂O. Found %: C 88.5; H 11.9. C₁₀H₁₆. Calculated %: C 88.3; H 11.7.

The terpene contained a small impurity of unsaturated hydrocarbon: 15.5 g of Fraction II was dissolved in 50 ml of pure acetone, and to the solution was added a 1% acetone solution of permanganate; very rapid reduction occurred up to 17 ml, then more slowly, and at 24 ml there was no decolorization after 20 minutes. The manganese dioxide was filtered off with suction, the solution diluted with water, the terpene filtered off suction, dried over potassium hydroxide, and distilled from the flask through a fractionating column. It distilled almost completely at 148-148.5°, m.p. 110-111°. At the same time, the oxidizability of bornylene was verified by the Meerwein method [6]; the weighed portion was 0.598 g, which reduced rapidly 38 ml, the experiment then being terminated.

The residue from the first distillation (18.4 g) was fractionated at 13 mm, and distilled almost completely at about 180°, solidifying completely in the container. After three recrystallizations from ethanol, a stable m.p. was attained, 78-79°.

0.1002 g substance: 0.3273 g CO₂; 0.1010 g H₂O. Found %: C 89.1; H 11.2. (C₁₀H₁₆)₂. Calculated %: C 88.9; H 11.1

The substance in acetone solution did not reduce the permanganate. It was recognized as dineotricyclenyl.

750 ml of an ether solution of the organomagnesium compound was oxidized with oxygen, 20 liters of oxygen being absorbed, the absorption then slowing down sharply. The reaction product was decomposed with water and weak acetic acid to a neutral reaction to litmus, the ether layer removed, dried with potash, and the ether distilled in a column of 8-10 theoretical plates, weight of the residue being 183 g. From this 33.3 g of neotricyclene was sublimed at 15 mm, and added to the above synthesized. The residue was distilled at 17 mm, the main fraction boiling at 100-102°, solidifying immediately in the container (alcohol); the next narrow fraction boiled at 172-175° at 15 mm, solidifying completely in the receiver, and after a double recrystallization from alcohol, melted at 78-79°, (dineotricyclenyl).

Fraction 100-102° at 17 mm was filtered off with suction from a small quantity of liquid, white crystals with camphor aroma, m.p. 132-145°, quite readily dissolved by all organic solvents, for example, 69 g dissolved in 15 ml of ethyl alcohol, and did not crystallize out upon cooling to -23°. Crystallization was successful from acetone or methyl acetate upon evaporation of the solvent by standing in open conical flasks; in the case of acetone, a constant m.p. was reached at 159-160°, and in the case of methyl acetate, 160-161°, long flat, lustrous needles.

0.1705 g substance: 0.3485 g CO₂; 0.1160 g H₂O. Found %: C 79.1; H 10.2. C₁₀H₁₆O. Calculated %: C 78.9; H 10.5.

Acid Phthalic Neotricyclenol Ester. The ester did not result in boiling benzene, the alcohol apparently not being primary; 2 g of the alcohol, 2 g of phthalic anhydride and 20 ml of xylene were heated for 2 hours at boiling temperature, water then added and the cooled reaction product neutralized with alkali to phenolphthalein. The aqueous layer was separated, filtered, and acidified with hydrochloric acid. A rapidly crystallizing oil resulted (3.8 g). The crystals dissolved completely in 50 ml of hot gasoline (b.p. 70-100°), needles resulting upon cooling. A third and fourth crystallization gave crystals with m.p. 104-105°.

0.1568 g substance: 5.23 ml 0.1 N alkali. Found: g-equiv. 301. C₁₂H₂₀O₄. Calculated: g-equiv. 300.

Phenylurethane of Neotricyclenol. 2 g of the alcohol and 4 g of phenylisocyanate were sealed together and heated for 7 hours at 80°, the excess of phenylisocyanate then being distilled off in vacuo, the solidified residue ground with water, and after 24 hours pressed out on paper and recrystallized from gasoline to an unchanging m.p. of 94-95° (hard prisms, four recrystallizations).

Hydrogenation of Neotricyclene. 32 g of the terpene with m.p. 110-111°, 80 ml of glacial acetic acid and 2 ml of 50% sulfuric acid were heated on a reflux (bath temperature 60°) to the cessation of terpene sublimation (6 hours), 20 ml of water was added to the reaction product, extraction with petroleum ether was carried out, followed by drying with potash and fractionation. 37.5 g of liquid fraction resulted with b.p. 117-118° at 23 mm. It was saponified by 6 hours boiling with an alcoholic (80 ml) solution of 15 g of potassium hydroxide; after dilution with water, the solid alcohol (28.1 g) was filtered off by suction and recrystallized from benzene. After a third recrystallization, there was attained a constant m.p. of 185.5-186°.

0.1151 g substance: 0.3295 g CO₂; 0.1233 g H₂O. Found %: C 78.1; H 11.9. C₁₀H₁₆O.
Calculated %: C 77.9; H 11.7.

In composition and melting point, the alcohol could be considered to be the neoborneol or the epiborneol.

Phenylurethane of the Alcohol. 1 g of the alcohol and 0.8 g of phenylisocyanate were sealed and heated for 1 hour on a boiling water bath. Everything solidified completely. After three recrystallizations from gasoline with b.p. 75-90°, there was obtained an unchanging m.p. of 138-139°. Melting point of the neoborneol phenylurethane was 140-141° [4], the epiborneol, 94-96° [7]. The alcohol can be considered to be neoborneol.

Oxidation of the Alcohol to the Ketone. 10 g of alcohol was dissolved in 100 ml of ether, and to this solution with water cooling and stirring there was added a solution of 4.5 g of chromic anhydride and 7 g of sulfuric acid in 60 ml of water; the ether and ketone were then flushed out with steam, and ether removed from the ether layer of the distillate, weight of the solid residue being 8.4 g. It did not give aldehyde reactions, was readily dissolved by all solvents, and after drying over sulfuric acid, gave an m.p. of 162-171°.

The Oxime of the Ketone. 1 g of the ketone, 1 g of hydroxylamine hydrochloride and 1 g of sodium hydroxide in 18 ml of alcohol were heated to boiling for 1 hour. The solution was then diluted with water and neutralized to phenolphthalein. The oxime was pressed out on paper and distilled with steam. The crystalline distillate in the condenser, after drying over sulfuric acid, melted at 98-110°. Two recrystallizations from alcohol raised the m.p. to 115-117°, a third did not change the melting point. The oxime of the camphor had an m.p. of 117°, the oxime of epicamphor an m.p. of 94°.

The bromoketone [8] was obtained from 3 g of the alcohol; after four recrystallizations from gasoline-ether mixture, an unchanging m.p. of 74-76° was attained. The m.p. of the bromocamphor was 76°, of the bromoepicamphor, m.p. 133°. The initial alcohol was found to be neoborneol. By the same fact structure (XI) was proven for the neotricyclene. Since the camphene dichloride, upon interaction with sodium, also gives the neotricyclene (XI), the structure 2,10-dichlorocamphene (see above) should be assigned to the dichloride

Oxidation of Neotricyclenol to the Corresponding Ketone.

A solution of 7 g of chromic anhydride and 10.5 g of sulfuric acid in 57 ml of water was added to 11.5 g of the alcohol with m.p. 156-158° in 50 ml ether, with stirring and cooling. The reaction product was then flushed out with steam, and the residue (6.3 g) obtained from the ether layer of the distillate after drying with potash and removing the ether, was fractionated. 4.5 g of solid product, with b.p. 200-205°, resulted. After pressing out on paper and drying over solid potassium hydroxide, m.p. 142-144°. The substance had a camphor odor and was quite rapidly volatilized; it did not give aldehyde reactions. Its semicarbazone resulted by 2 hours of boiling with an alcoholic solution of semicarbazide acetate, and brought crystallization from benzene to a stable melting point of 208-209°.

Hydration of Neotricyclenol to Camphanediol-2, 10.

23 g of the alcohol with m.p. 156-158°, 60 ml of acetic acid and 1.5 ml of 50% sulfuric acid were heated on a boiling water bath for 6 hours, and then after diluting with water to 300 ml, unreacted alcohol was distilled out of the solution with steam, 3.5 g was distilled, m.p. 152-158°.

The aqueous solution was evaporated in vacuum to 100 ml, crystals and oil resulting, crystals (13.5 g) not neutralizing alkali upon boiling, the oil (4 g) neutralizing. Evidently, upon distilling with steam in the presence of sulfuric acid, the dioldiacetate saponified completely. The oil was saponified by boiling with alkali, the

reaction product solidifying. It, and the first crystals, were crystallized separately from the aqueous solution to an unchanging m.p. of 172-173° (four recrystallizations).

0.1286, 0.1265 g substance: 0.3327, 0.3266 g CO₂; 0.1246, 0.1221 g H₂O. Found %: C 70.6, 70.4; H 10.8, 10.8. C₁₅H₁₈O₂. Calculated %: C 70.6; H 10.6.

Oxidation of Camphanediol-2,10. 2.6 g of the diol in 300 ml of water was oxidized on a boiling bath by addition of a 3% solution of permanganate to a pink color stable for 30 minutes. 315 ml, i.e., about 9.45 g of KMnO₄ was used. The manganese dioxide was filtered off with suction, the alkaline solution evaporated to 50 ml and acidified with hydrochloric acid to Congo red. 1.38 g of crystals (hard prisms) resulted, with m.p. 207-210°, and an equivalent weight of 185 (0.0848 g of substance, 4.57 ml of 0.1 N alkali). By repeated crystallizations from aqueous alcohol, it was possible to bring the melting point to 217-219°, equivalent weight 183 (ketopinic acid, m.p. 232°, equivalent weight 182). Since ketopinic acid gives carboxyapocamphoric acid, of m.p. 199-201° and equivalent weight 76.6, with nitric acid (sp. gr. 1.40), all fractions, including the crystallized 1.38 g of primary precipitate, and the 1.25 g of acids, with m.p. 198-206°, extracted with alcohol from the mother liquor from the first precipitation, were heated with 20 ml of nitric acid (sp. gr. 1.40) to cessation of nitrogen oxide evolution (12 minutes). 1.45 g of needle crystals precipitated from the cooled solution. They were filtered off by vacuum, washed with a small quantity of water, and dried at 100° to constant weight. M.p. 199-201°, with the evolution of carbon dioxide, equivalent weight 75.7 (0.0614 g of the substance, 8.1 ml of 0.1 N alkali). The acid was found to be the carboxyapocamphoric.

SUMMARY

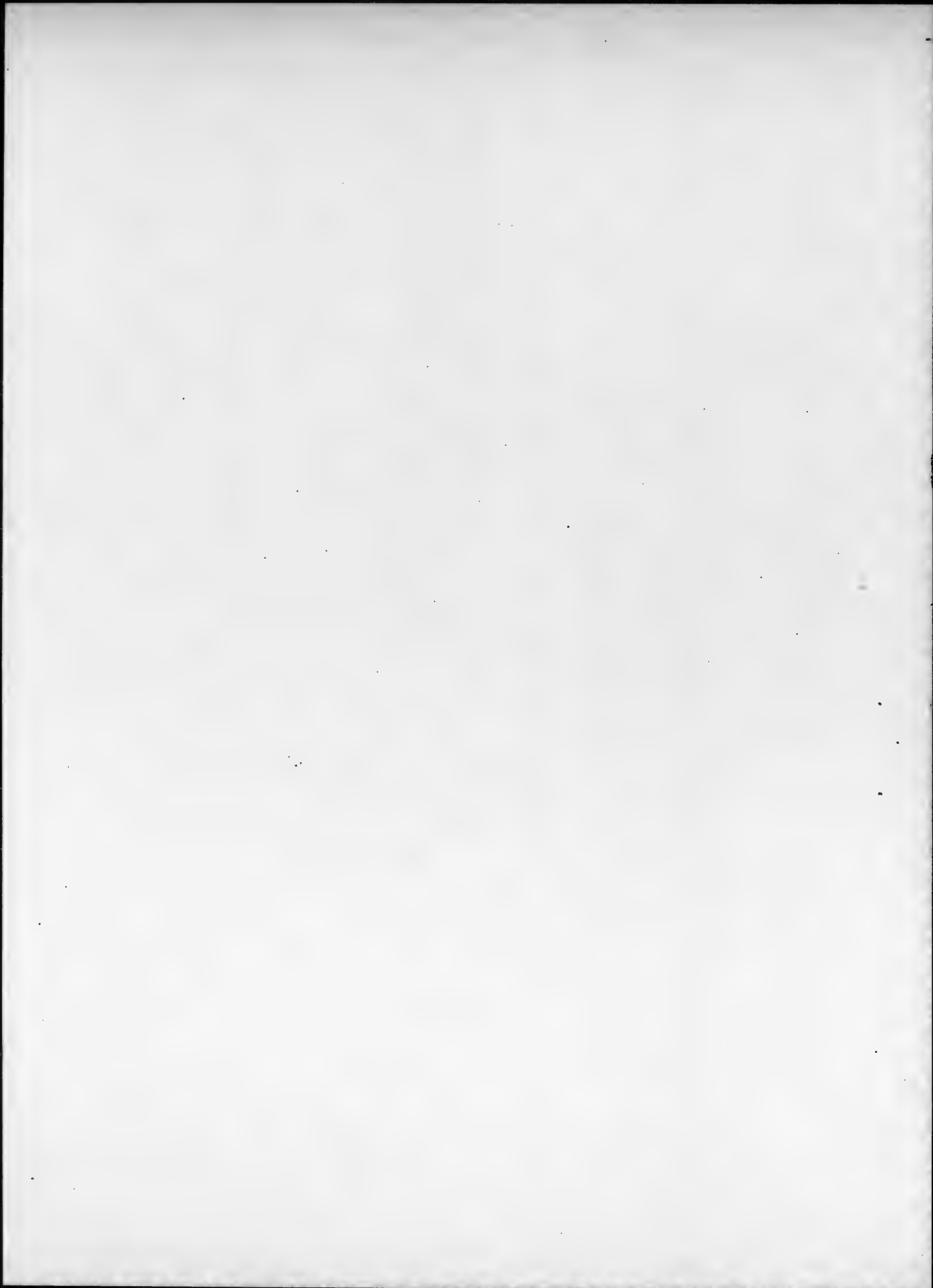
1. The structure of camphene dichloride has been studied, and it has been demonstrated to be 2,10-dichlorocamphane. Its formation from camphene proceeds with retropinacolinic rearrangement, which permits a deduction relative to polarization of the chlorine molecule at the moment of its reaction with the double bond of camphene.
2. Upon interaction with excess sodium, 2,10-dichlorocamphane gives camphane, neotricyclene (XI) and some bornylene.
3. Removal of a hydrogen chloride molecule from 2,10-dichlorocamphane at the present time indicates a chloride of either neotricyclene (VI), or of (VIII).
4. Decomposition of the organomagnesium compound from (VI) or (VIII) with water gives neotricyclene (XI), unknown up to the present time, and oxidation of the organomagnesium compound with oxygen gives a new tricyclic alcohol, with m.p. 159-160°.
5. Hydration of this alcohol gives camphanediol-2,10, not described until now.

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Received February 11, 1953

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THE PROBLEM OF METALLOORGANIC COMPOUND FORMATION BY INTERACTION OF AN AROMATIC SILANE WITH METAL CHLORIDES

III. FORMATION OF THE ORGANOANTIMONY COMPOUND BY INTERACTION OF PHENYL CHLOROSILANE WITH SbCl_5

A. Ya. Yakubovich and G. V. Motsarev

It was mentioned earlier that the interaction of phenylchlorosilanes with AlCl_3 [1], and in some cases with FeCl_3 [2], is accompanied by rupture of the $\text{Si}-\text{C}$ bond, with simultaneous formation of the aromatic aluminum-, and, evidently, unstable organoiron compounds. It was of interest, therefore, to explain the relationship of phenylchlorosilanes to the chlorides of antimony (SbCl_3 and SbCl_5), whose interactions have not hitherto been investigated.

Experiments have indicated that in contrast to AlCl_3 and FeCl_3 , SbCl_3 is not found to be a dearylating agent. In actuality, if, for example, diphenyldichlorosilane ruptures AlCl_3 or FeCl_3 at 30° , then SbCl_3 will not react with it, even at 200° .

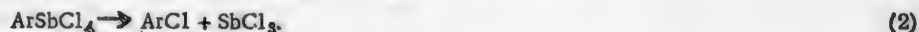
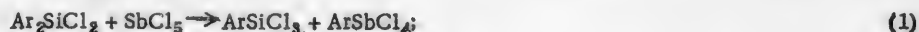
However, in the case of SbCl_5 it was found that rupture of diphenyldichlorosilane proceeds very readily at normal temperature. Upon mixing diphenyldichlorosilane, both in molar ratio and with excess SbCl_5 (2 moles), intense reaction is observed, accompanied by heat evolution and appearance of orange coloration. The products of this reaction were found to be phenyltrichlorosilane, chlorobenzene and SbCl_3 . This indicated that SbCl_5 reacts with a molecule of diphenyldichlorosilane with rupture of the $\text{Si}-\text{C}$ bond only, independently of the presence of SbCl_5 excess. The latter was also confirmed by special experiments on the study of the interaction of phenyltrichlorosilane with SbCl_5 , which have demonstrated that reaction between them does not occur, even with heating.

Analogous results were observed for the reaction of SbCl_5 with di-(p-chlorophenyl)-dichlorosilane, and also as obtained by organomagnesium synthesis:



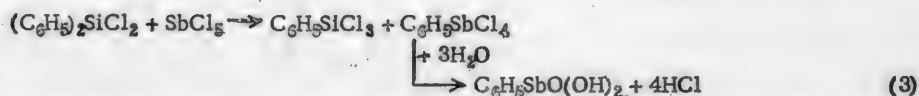
at normal temperature. From the reaction products in this case were obtained p-chlorophenyltrichlorosilane (identified by the corresponding resin), p-dichlorobenzene and SbCl_3 .

A comparison of the results obtained made it possible to assume that rupture of diphenyldichlorosilane and its halogen derivatives by antimony pentachloride proceeds according to Equation (1), with formation of an intermediate, unstable under normal conditions, organoantimony compound, readily decomposed at the $\text{C}-\text{Sb}$ bond according to Equation (2) (Ar = Aromatic radical).



This assumption was successfully proved by experiment.

If rupture is carried out at lowered temperature (-20°), then formation, for example, of phenylstibintetrachloride, resulting from such procedure, can be easily proved by conversion to phenylstibinic acid, which was isolated in a yield of 55% of theory.



Consequently, the described interaction of aromatic silanes with SbCl_5 proceeding readily under the conditions described is found to be a new synthetic method for aromatic stibines.

Thus, the accuracy of the proposed rupture mechanism of diphenyldichlorosilane and its derivatives of SbCl_5 under normal conditions, as indicated in Equations (1) and (2), is confirmed not only by the possibility of isolating the corresponding silicon-containing rupture products of phenylchlorosilane, but also by the proved formation of intermediate organoantimony compounds.

It is indeed obvious that the interaction of phenylchlorosilanes and their derivatives with SbCl_5 proceeds according to a mechanism similar to the interaction mechanisms of phenylchlorosilanes with AlCl_3 and FeCl_3 . Actually, in the case of all three of these chlorides, the rupture of aromatic silanes by them proceeds very easily, and the reaction products are found to be on the one hand silicon-containing compounds (SiCl_4 and $\text{C}_6\text{H}_5\text{SiCl}_3$), and on the other, organic compounds of aluminum, antimony or iron.

According to their dearylating activity, the indicated chlorides can be arranged in the following decreasing order $\text{AlCl}_3 > \text{FeCl}_3 > \text{SbCl}_5$, according to which there is observed this or some other degree of ease of rupture at the C-Si bond of aromatic silanes.

EXPERIMENTAL

Interaction of Diphenyldichlorosilane with SbCl_5

5.25 g (0.023 mole) of antimony trichloride, purified beforehand by vacuum distillation, was added to 5 g (0.02 mole) of diphenyldichlorosilane. The mixture was heated for 7 hours at 150-200°, after which the reaction products were distilled in vacuo. The resulting fractions were: 1) b.p. 80-90° at 6 mm - 5.0 g; 2) b.p. 90-135° at 6 mm - 0.3 g; 3) b.p. 135-145° at 6 mm - 4.3 g. There remained in the residue 0.5 g of dark resin.

Upon standing, the first fraction crystallized; upon repeated distillation, 4.6 g of antimony trichloride was isolated. The antimony found was 53.0%, theory 53.3%. Upon repeated distillation of the 3rd fraction, 4.0 g of colorless liquid resulted, with a sharp odor, and b.p. 142-144° at 6 mm, representing unchanged diphenyldichlorosilane.

Found %: Cl 27.8; Si 11.0. $\text{C}_{12}\text{H}_{10}\text{SiCl}_2$. Calculated %: Cl 28.0; Si 11.07.

Interaction of p,p'-Dichlorodiphenyldichlorosilane with SbCl_5

6.0 g (0.02 mole) of antimony pentachloride was added gradually to 5.0 g (0.021 mole) of p,p'-dichlorodiphenyldichlorosilane. Upon mixing the reactants, a strong heat evolution (up to 80°) was observed in the reaction mass, with a color change to orange. After addition of the total amount of antimony pentachloride, the mixture was heated for 5 hours at 80-90°. The reaction product was distilled in vacuo, wherein a fraction with b.p. 70-105° at 13 mm was isolated in the amount of 7.5 g, which, upon standing, crystallized partially. The crystals which separated from the liquid portion upon cooling to 0° were found to be antimony trichloride (3.0 g). The liquid portion was treated with water and distilled with steam. The water distillate contained crystals which, after separation from water, and recrystallization from petroleum ether, had a m.p. of 53°, and were p-dichlorobenzene.

Found %: Cl 48.1. $\text{C}_6\text{H}_4\text{Cl}_2$. Calculated %: Cl 48.3. Yield 1.8 g, 78% of theory.

The residue in the distilling flask was a transparent resin, which from its chlorine and silicon contents, corresponded to the resin isolated from monochlorophenyltrichlorosilane.

0.1210, 0.1276 g substance: 0.1078, 0.1131 g AgCl (Carius). 0.2001, 0.2090 g substance: 0.0723, 0.0759 g SiO_2 . Found %: Cl 22.1, 22.0; Si 16.9, 17.0 ($\text{C}_6\text{H}_4\text{ClSiO}_{1.5}$)_n. Calculated %: Cl 21.7; Si 17.1

From the quantity of reaction products isolated, it follows that rupture of p,p'-dichlorodiphenyldichlorosilane by antimony pentachloride under the conditions given, proceeded on the average to 80% completion.

Interaction of Diphenyldichlorosilane with SbCl_5

a) At a decreased temperature (-20°). Synthesis of phenylstibinic acid. 5.9 g (0.0196 mole) of antimony pentachloride, precooled to -20°, was gradually added to 5.0 g (0.0197 mole) of diphenyldichlorosilane, also precooled to -20°. The reaction mass, at first dark-green in color, rapidly changed to dark-orange.

The mixture was twice treated with concentrated hydrochloric acid saturated with hydrogen chloride, with cooling, to remove antimony trichloride, the formation of which was to be expected because of partial rupture of phenylstibinetetrachloride. The hydrochloride solution, upon dilution with water, produced a white precipitate of antimony oxide, soluble in concentrated hydrochloric acid.

Subsequent treatment of the mixture with water, and cooling, led to formation of a copious precipitate, white in color, and a viscous tar, which was extracted with ether. The ether layer was separated, and the ether distilled off. After distilling off the ether, 2.0 g (78.4% of theory) resulted of the resin, which corresponded in analysis of silicon content to the resin which resulted from phenyltrichlorosilane. The silicon found was 20.9%, in theory 21.7.

The white-colored precipitate contained in the water layer (after separation of the ether layer) was filtered off, washed several times with ether, then with water, and dried. From an analysis of the antimony content (found 50.1%; theory, 49.83%), and from the properties (an amorphous powder, insoluble in water, soluble in aqueous ammonia, soda, alkaline hydroxide and in glacial acetic acid), the substance corresponded to phenylstibinic acid. 2.7 g, or 55% of theory, resulted.

b) At normal temperature. 23.6 g (0.079 mole) of antimony pentachloride was gradually added to 10.0 g (0.039 mole) diphenyldichlorosilane. There occurred a strong heat evolution in the mixture, and formation of a dark-orange color. After suitable treatment (see preceding experiment), 15.5 g of antimony trichloride and 3.6 g of a liquid with b.p. 130-131° resulted, identified from its boiling point and density (d_4^{20} 1.1069) as chlorobenzene. The chlorine found was 31.1%, theory 31.5. The yield of chlorobenzene was 81.4% of theory.

The residue in the distilling flask after distilling with steam was a transparent resin, which, by analysis, of the silicon content, corresponded to the resin which resulted from phenyltrichlorosilane. The silicon found was 21.3%, theory 21.7%.

SUMMARY

1. The interaction of antimony trichloride and of pentachloride with phenyltrichlorosilane, diphenyldichlorosilane and its p,p'-dichloroderivative have been studied

It has been found that in contrast to the primary chlorosilanes, the secondary are very easily ruptured by antimony pentachloride, in such a manner that the primary aryltrichlorosilane is formed, the antimony trichloride splitting the aryl radical from it, thus transforming to the corresponding chloroderivatives.

2. It has been proved that the mechanism of the above-indicated interaction of arylchlorosilanes with antimony pentachloride consists of a disproportionation reaction between them, which is accompanied by the formation of an unstable arylstibinetetrachloride, which decomposes under normal conditions into antimony trichloride and the arylchloride.

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Received October 7, 1952.

* See Consultants Bureau Translation, page 805.

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INVESTIGATION OF THE ALKALOIDS OF SENECIO SPECIES

VIII. ALKALOIDS FROM THE SPIRAL RAGWEED (SENECIO SARRACENIUS)

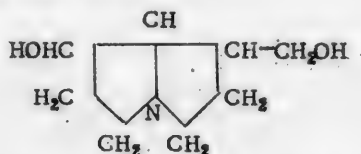
A. Danilova, R. Konovalova, P. Massagetov and M. Garina

In the author's laboratory, investigations have been carried out chiefly upon various species of ragweed growing in the Caucasus and in Middle Asia. A study of the alkaloids isolated from various species of ragweed [1] is without doubt of theoretical and practical import. Suffice to point out that platiphyllin [2] from the broadleaf ragweed is used in medical practice as a spasmolytic and as an agent for decreasing blood pressure. It was, therefore, of interest to study various species of ragweed growing in other regions of the Soviet Union. In 1949, the VNIKhFI* expedition, under the leadership of P. S. Massagetov, collected in the Altai the above-ground portions of spiral ragweed (Senecio sarracenus) during the blossoming phase. The plant was collected on the banks of the River Bukhtarma in August. This perennial grassy plant is wide-spread in the area of water basins. It occurs in Western Europe, the European section of the USSR, and in Siberia.

The spiral ragweed contains considerable quantities of alkaloids, from 0.8 to 0.9%. Isolation of the alkaloids was carried out by the usual method, namely, by extracting the plant with dichloroethane, moistened beforehand with ammonia, and by extracting the bases from the alkaline solution, first with ether, and then with chloroform. A mixture of alkaloids resulted from the ether solution in the form of a viscous mass. The crystalline bitartrate of a base, having an m.p. of 177-179°, was obtained from the mixture using an alcoholic solution of tartaric acid. An anhydrous base was obtained from the bitartrate in the form of a colorless liquid, turning yellow rapidly in the light. Upon mixing with several drops of water, the base converted to a powder. After recrystallizing from water, m.p. 51-52°, $[\alpha]_D -129.7^\circ$. The composition of the anhydrous base was $C_{18}H_{27}O_5N$. In composition, the base isolated was isomeric with platiphyllin, but not identical with it. From its properties, and also from the properties of the salts, the alkaloid isolated differed from the bases described, and was named "sarracin" by the authors. Sarracin is readily soluble in alcohol, ether, chloroform, poorly so in water, forming a crystalline picrate, m.p. 140-141°. It contains an hydroxyl group, and does not contain the methylimidine group. It decolorizes readily a solution of potassium permanganate. As with other alkaloids isolated from various ragweed species, sarracin has the properties of an ester. Upon heating with alkali, it decomposes into an aminoalcohol and organic acids.

The aminoalcohol is a crystalline compound with m.p. 151-152° and $[\alpha]_D -57^\circ$ (c = 1.4 in $CHCl_3$). It decomposes readily in water, alcohol, is poorly soluble in chloroform, and is almost insoluble in ether and petroleum ether. It forms a picrate with m.p. 184-185°. The properties of the aminoalcohol and of its salts coincide exactly with the properties of platinecine, which was obtained by R. A. Konovalova and A. P. Orekhov by hydrolysis of platiphyllin. By direct comparison of both bases, the authors have established their exact identity.

As the result, the aminoalcohol resulting from hydrolysis of sarracin has been found to be platinecine [3], for which the following structure has been established:



The unsaturated properties of sarracin are explainable by the presence of a double bond in the esterifying acids. Thus, sarracin differs from platiphyllin by the nature of the esterifying acids.

Considering the fact that the alkaloids separated from various ragweed species, and the closely-related alkaloids from heliotropium, are frequently found in plants as the N-oxide form, it can be assumed that N-oxides of the

* All-Union Chemico-Pharmaceutical Institute of Scientific Research.

alkaloids in spiral ragweed are also present. In fact, by extracting the alkaloids from the plant by chloroform, without ammonia pre-moistening, the authors isolated a substance which possessed an almost neutral character, whereas alkaloids possessing basic properties that were present as salts in the plant were not extractable by chloroform. In this way, a second alkaloid of the composition $C_{18}H_{27}O_5N$ was isolated, containing one more oxygen than sarracin. This new alkaloid, after recrystallization from acetone, had an m.p. of 123-124° and $[\alpha]_D -81.65^\circ$. It dissolved readily in water and alcohol, and with great difficulty in ether. It formed a crystalline picrate with m.p. 107.5-108.5°, and a chloroaurate with m.p. 153-155°. Upon reduction with zinc dust in hydrochloric acid medium, it converted to sarracin.

All of the indicated properties of the newly isolated alkaloid permitted the assumption that an oxygen atom is directly connected with nitrogen in the molecule, and is therefore the N-oxide of sarracin. To confirm the accuracy of this assumption, the N-oxide of sarracin was synthesized by reacting sarracin with hydrogen peroxide. A direct comparison of the substance resulting by this procedure with the N-oxide of sarracin demonstrated their complete identity.

The authors found by further work that total alkaloid extraction from spiral ragweed is more convenient with isopropyl alcohol acidified with acetic acid. Under these conditions, isopropyl alcohol also extracts the N-oxide form of sarracin as well as sarracin itself. Reduction of the total isolated bases with zinc dust in hydrochloric acid medium gave sarracin in an amount sufficient for additional study.

EXPERIMENTAL

Isolation of the Alkaloids. Dry, finely powdered plant, in the amount of 17 kg, was exhaustively extracted with isopropyl alcohol, to which was added acetic acid (2% to the volume of alcohol). The alcohol was distilled off in vacuo to a residue of thick consistency. The latter was dissolved in benzene. The benzene solution was extracted several times with 10% sulfuric acid. The acid solutions were combined, filtered, washed in a separatory funnel, first with benzene and then with ether. The hydrochloride solution of alkaloids was alkalinized with 25% ammonia, with cooling, to an alkaline reaction for phenolphthalein, and extracted with ether. By this procedure a considerable portion of the sarracin (I) converted to the ester.

The aqueous solution was then extracted with ether, acidified with sulfuric acid to an acid Congo reaction, and reduced with zinc dust, using mechanical stirring. The acid solution resulting from reduction of the N-oxide was alkalinized with ammonia and extracted, first with ether (II) and then with chloroform (III). The ether solutions (I) and (II) were combined and dried over Na_2SO_4 . After distilling off the ether, 147 g of alkaloids resulted in the form of a light-brown colored viscous mass.

The chloroform solution (III) was dried over Na_2SO_4 . After distilling off the chloroform, 18 g of dark-brown colored resinous bases resulted. It was not possible to obtain any characteristic salts.

Synthesis of the Sarracin Salts. The 147 g of alkaloids obtained after distilling off the ether were dissolved in 120 ml of alcohol, and to the alcoholic solution was added 80 g of tartaric acid dissolved in 200 ml of alcohol. The mixture was heated to boiling on a reflux. The resulting sarracin bitartrate was filtered off with suction and washed with alcohol. After three crystallizations from alcohol, 1:10, 40 g of sarracin bitartrate resulted with m.p. 177-179°. An additional 10 g of sarracin bitartrate was isolated from the mother liquors.

0.2455 g substance: in 4.5 ml water; $\alpha_D -1.91^\circ$, $[\alpha]_D -70.05^\circ$; $d_{20} 1.05$ dm. 3.796 mg substance: 7.556 mg CO_2 ; 2.315 mg H_2O . 4.499 mg substance: 8.884 mg CO_2 ; 2.716 mg H_2O . 8.295 mg substance: 0.218 ml N_2 (26.0°, 732.0 mm). 9.215 mg substance: 0.239 ml N_2 (22.0°, 734.0 mm). Found %: C 54.29, 53.89; H 6.82, 6.75; N 2.89, 2.91. $C_{18}H_{27}O_5N \cdot C_4H_6O_6$. Calculated %: C 54.20; H 6.77; N 2.87.

Isolation of Sarracin Base from the Bitartrate. 10 g of sarracin bitartrate was dissolved in 50 ml of water. The aqueous solution was alkalinized with 25% ammonia in the presence of ether. The sarracin base which separated out in the form of colorless oily drops readily dissolved in ether. The ether solution was filtered. 6.5 g of sarracin resulted after distilling off the ether. After recrystallizing twice from water, sarracin resulted with m.p. 50-52°.*

0.4450 g substance. in 4.5 ml alcohol; $\alpha_D -12.83^\circ$; $[\alpha]_D -129.7^\circ$; $d_{20} 1.1$ dm. 4.890 mg substance: 11.507 mg CO_2 ; 3.581 mg H_2O . 8.900 mg substance: 0.327 ml N_2 (21.0°, 738.5 mm). 14.260 mg substance: 0.531 ml N_2 (26.5°, 730.0 mm). 5.971 mg substance: 0.47 ml CH_4 (26.0°, 751.0 mm). 5.144 mg substance: 0.39 ml CH_4 (26°, 748.0 mm). Found %: C 64.17; H 8.19; N 4.15, 4.07; OH 5.50, 5.30. $C_{18}H_{27}O_5N$.

* For analysis the compound was taken on the basis of water of crystallization.

Calculated %: C 64.09; H 8.01; N 4.15; OH 5.04.

Sarracin Picrate. 2.8 g of sarracin base was dissolved in 15 ml of alcohol. Picric acid was added to the saturated alcoholic solution. The sarracin picrate which separated out was filtered with suction and washed with alcohol. After 2 recrystallizations, from alcohol (1:3), the m.p. of the picrate was 140-141°.

2.855 mg substance: 5.339 mg CO₂; 1.379 mg H₂O. 4.785 mg substance: 0.418 ml N₂ (24.5°, 736.0 mm). Found %: C 51.03; H 5.39; N 9.92. C₁₈H₂₇O₆N · C₆H₃O₇N₃. Calculated %: C 50.88; H 5.30; N 9.87.

Extraction of Sarracin N-oxide from the Plant. The alkaloids were exhaustively extracted by chloroform from 700 g of pulverized plant. The chloroform extracts were combined and extracted with 10% sulfuric acid. The acid solution was filtered off and alkalized with ammonia, with cooling. The alkaloids from the alkaline solution were extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate. After distilling off the chloroform, 1.8 g of alkaloids resulted, which constituted 0.25% of the total plant weight taken. After 3 recrystallizations from acetone, the m.p. of the sarracin N-oxide was 123-124°. The oxide was readily soluble in water and alcohol and poorly so in ether and acetone.

0.4542 g substance in 4.5 ml water, $\alpha_D -4.12^\circ$, $[\alpha]_D -81.65^\circ$; l 0.5 dm, 5.395 mg substance: 0.196 ml N₂ (23.5°, 731.0 mm). Found %: N 4.02. C₁₈H₂₇O₆N. Calculated %: N 3.96.

Sarracin N-Oxide Picrate. Sarracin N-oxide in the amount of 1.5 g was dissolved in 5 ml of alcohol. A saturated alcoholic solution of picric acid was added to the solution. The picrate separated out as a precipitate upon rubbing with a glass rod. After recrystallizing three times from alcohol, m.p. was 107.5-108.5°.

2.990 mg substance: 5.364 mg CO₂; 1.424 mg H₂O. 0.355 mg substance: 0.378 ml N₂ (22.0°, 736.0 mm) 4.845 mg substance: 0.423 ml N₂ (26.5°, 740.00 mm). Found %: C 48.96; H 5.33; N 9.73, 9.69. C₁₈H₂₇O₆N · C₆H₃O₇N₃. Calculated %: C 49.48; H 5.15; N 9.62.

The Chloroaurate of Sarracin N-Oxide. Sarracin N-oxide in the amount of 0.2 g was dissolved in 5 ml of 10% hydrochloric acid, to which was added an aqueous solution of H₂SO₄. The resulting chloroaurate precipitate was filtered off with suction and washed with hydrochloric acid. After one recrystallization from acidified water, the m.p. was 153-155°. The chloroaurate of the N-oxide is an unstable salt. With heating and upon long standing in the light, it decomposes readily.

3.626 mg substance: 1.059 mg Au. 5.555 mg substance: 1.607 mg Au. Found %: Au 29.20, 28.93. C₁₈H₂₇O₆N · H₂SO₄. Calculated %: Au 28.45.

Reduction of Sarracin N-Oxide with Zinc Dust. Sarracin N-Oxide in the amount of 0.5 g was dissolved in 10 ml of 10% sulfuric acid. 2 g of zinc dust was gradually added to the solution with stirring. The resulting solution was filtered, alkalized with ammonia and extracted with ether. After distilling off the ether, 0.3 g of sarracin resulted with m.p. 41-42°. Due to difficulty in purifying and identifying sarracin as the base, the bitartrate was obtained. The latter, after recrystallization from alcohol, melted at 177-178°, and did not give depression in melting point with sarracin bitartrate isolated from the plant.

Oxidation of Sarracin with a 3% Solution of Hydrogen Peroxide. 12 ml of 3% hydrogen peroxide was added to 1.3 g of sarracin base. The mixture was left at room temperature for 48 hours. After lapse of the indicated time, all of the substance went into solution. The acid aqueous solution was alkalized with ammonia, with cooling, and extracted with ether. Non-oxidized sarracin went into the ether. After extraction with ether, the aqueous solution was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate. After distilling off the chloroform, 0.38 g of substance, with m.p. 122-123°, was obtained, which did not give depression in melting point with sarracin N-oxide isolated directly from the plant.

Hydrolytic Rupture of Sarracin. 50 ml of 0.5 N alcoholic potassium hydroxide solution was added to 4.3 g of sarracin, and the mixture boiled over reflux for 3 hours. The alcohol was distilled off to dryness. The residue was acidified with 10% sulfuric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate. After distilling off the ether, 2.5 g of viscous non-crystalline acid was obtained. The acid aqueous solution which remained after extraction with ether was alkalized with 25% alkali, and was then extracted first with ether and then with chloroform. The ether and chloroform solutions were dried over anhydrous sodium sulfate.

After distilling off the ether, 0.5 g of the liquid aminoalcohol resulted, which formed a crystalline picrate, m.p. 264-266°, with an alcoholic solution of picric acid. The properties of the liquid aminoalcohol and its picrate

coincided with the properties of anhydroplatinecin and the picrate of the latter. There was no depression upon determining the melting point of a mixture of the liquid aminoalcohol picrate from the spiral ragweed with anhydroplatinecin picrate. After distilling off the chloroform, 1.2 g of crystalline aminoalcohol resulted with m.p. 146-149°. After 2 recrystallizations from acetone, m.p. 151-152°. Readily soluble in water and alcohol, poorly so in acetone and ether, almost insoluble in petroleum ether. With an alcoholic solution of picric acid, it formed a crystalline picrate with m.p. 184-185°.

The specific rotation of the aminoalcohol was $[\alpha]_D^{25} -85.16^\circ$ ($c = 1.22$, in alcohol); $[\alpha]_D^{25} -57^\circ$ ($c = 1.4$, in CHCl_3).

No depression was observed in determining the melting point of a mixture of the aminoalcohol from spiral ragweed with platinecin obtained by saponification of platiphyllin, nor for a mixture of their picrates.

Analyses were carried out in the microanalytical laboratory of VNIKhFI under the supervision of V. V. Kolpakova.

SUMMARY

1. Two new alkaloids, sarracin $\text{C}_{18}\text{H}_{27}\text{O}_5\text{N}$, and sarracin N-oxide, $\text{C}_{18}\text{H}_{27}\text{O}_6\text{N}$, have been isolated from the spiral ragweed (Senecio sarraceni).
2. It has been determined that sarracin represents an ester of platinecin and organic acids.
3. Sarracin picrate and bitartrate have been obtained, as well as the picrate and chloroaurate of sarracin N-oxide.

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Received January 27, 1953.

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* See Consultants Bureau Translation, page 1989.

SPECTROGRAPHIC INVESTIGATION OF CARDIAC GLYCOSIDES FROM HELLEBORE

M. Ya. Tropp, Yu. V. Shostenko and D. G. Kolesnikov*

The cardiac glycosides represent a group of rather valuable medicinal substances. Because of the complexity in structure, the ease of rupture, and the isomerizability of cardiac glycoside molecules, and also since they occur in very small amounts in plants, their chemical study, represented by a series of works (see reviews [1, 2]) is still far from complete.

The purpose of the present work was to utilize absorption spectra in the ultra violet for investigation of new cardiac glycosides, and to attempt their utilization for analytical determination of the latter. As the objects of investigation, new crystalline glycosides from the phyto-chemical laboratory of the Kharkov Scientific Research Chemical-Pharmaceutical Institute were taken by Kolesnikov and Tropp [3], from the roots of the caucasian (*Helleborus caucasicus* A. Br.) and the red (*Helleborus purpurascens* W. and K.) hellebores. The first of them was named corelborin K, and the second, corelborin P. A study of the two glycosides by the authors indicated [3], gave some grounds for belief that the two glycosides belong to glycosides of the scillarene group, isolated for the first time from a domestic raw material.

EXPERIMENTAL

Investigation of the absorption spectra for the cardiac glycosides, and their transformation products, was carried out with the help of a quartz spectrograph ISP-22. An arc between the electrodes and tungsten steel served as the light source. The glucose solution was placed in a cell with variable absorption layer thickness. The solvents used were —water and ethyl alcohol —purified in an appropriate manner, and their optical transparency verified by spectrographic means in the 2200–4000 Å range. The original glycosides were pure, crystalline substances, of constant melting points.

To obtain the absorption curves, the authors took spectrograms based upon a minimal exposure time for the solvent [4]. Solutions of the substances investigated and the solvent were successively photographed at absorption layer thicknesses of 0.5, 1, 2, 2.5 and 5 cm. Exposure for the solvents was 10 seconds, and for the solutions; from 40 to 100 seconds.

X-ray film (with a sensitivity of 250, H and D) was used, which was placed in the spectrograph frame by a special holder to avoid bending. The photometry was carried out visually by means of a magnifying glass. For convenience in visual photometry, it is necessary that the solvent spectrum be situated in the photograph exactly beneath the solution spectrum (without any break between them). To meet this requirement, the authors prepared a special diaphragm with two horizontal openings, one shifted in relation to the other, and arranged in such a manner that the upper limit of one aperture went into the lower limit of the other.

The length of each aperture was 0.8 mm. The use of such an aperture ensured the obtaining of spectral pairs closely aligned to each other.

To eliminate possible errors, photographing of the absorption spectra was carried out from one direction by shifting the frame. In addition, to verify reproducibility of results, the same absorption curve was photographed and photometered several times. The concentration of solution investigated was 10^{-4} or 10^{-5} moles/liter.

EVALUATION OF RESULTS

Absorption curves for corelborin P and corelborin K in ethanol are given in Fig. 1. These curves have a characteristic maximum at 3000 Å, and a minimum at about 2475 Å. A similar maximum is also found for the absorption curves of hellebrin and desglucohellebrin glycosides from the black hellebore which were isolated and studied by Karrer and Schmutz [5]. These circumstances, together with the results of other experiments [3], have given the basis, as has already been indicated, for referring both glycosides to that group of glycosides which possesses a six-membered unsaturated lactone ring with 3 conjugated double bonds, inasmuch as the glycosides of

* S. Yanova participated in the experimental part of the work.

a five-membered lactone ring (two conjugated double bonds), according to both the literature [2] and the authors' data, (Fig. 1), have a characteristic maximum in the range 2200-2300 Å.

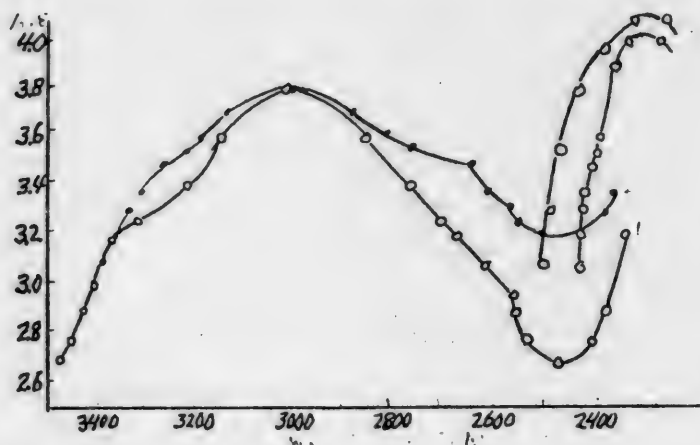


Fig. 1. Absorption Curves.

1) Corelborin K; 2) corelborin P; 3) convallatoxin; 4) convallaside.

of domestic manufacture, as isolated by the authors—convallatoxin and convallaside, differing from corelborin K and corelborin P only in the respect that they possess a five-membered lactone ring instead of a six-membered lactone ring. In this case, also in the range 2340-2500 Å, the convallaside absorption curve which contains one more sugar molecule than convallatoxin lies above the curve of the latter.

A comparison of the Fig. 1 curves shows clearly the extent to which the absorption spectra of cardiac glycosides depend upon the structure of the lactone ring. The introduction of one additional conjugated double bond shifts sharply the entire absorption curve into the long wave length region. This fact makes it possible to utilize absorption spectra as the principal and most reliable indication for classification of cardiac glycosides into a group containing the five-membered unsaturated lactone ring, and a group containing the six-membered ring, along with the sodium nitroprusside color reaction (in 1N NaOH), the sodium picrate (in neutral medium), and with acetic anhydride and sulfuric acid. It should be noted at the same time that it follows from the authors' and the literature data [2] that the absorption spectra of cardiac glycosides (or their aglucones) differ only by substituents in the ring (for the same sugars and same lactone ring), differing little from one another, and therefore cannot serve practically for identification of individual substances.

Cardiac glycoside molecules hydrolyze readily. In an acid medium this leads to splitting of the sugar component, but in an alkaline medium, however, depending upon conditions, leads to rupture of the lactone ring, or to more extensive changes in the molecule. It was of interest to follow by means of absorption spectra the hydrolysis of corelborin

The close similarity of the two curves presented in Fig. 1 speak for the close resemblance in structure of the two glycosides from hellebore; at the same time, however, they differ so much from each other (minimum position at 2475 Å) that there is no doubt about the fact that they belong to two different substances. The higher value, $\log \epsilon$, in the range of 2350-2750 Å for corelborin P is apparently related to the presence of an additional sugar molecule in the molecule (as compared to corelborin K), which increases the intensity of absorption in this range at the expense of additivity in absorption. In the same Fig. 1 absorption curves are given for two other individual glycosides

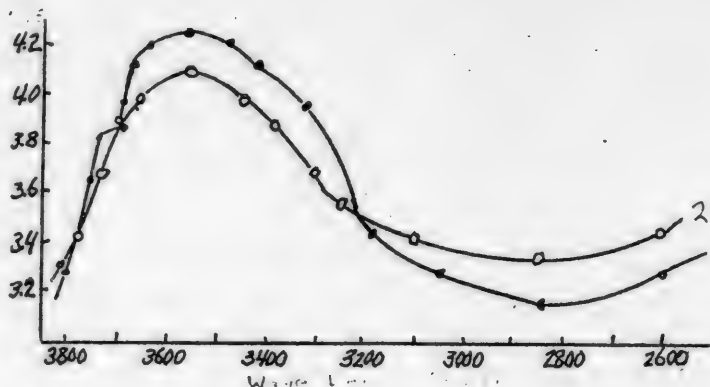


Fig. 2. Absorption Curves for Lactone Titration Products.

1) Corelborin K; 2) corelborin P.

K and corelborin P in alkaline medium. For this purpose, both glycosides were subjected to so-called lactone titration in 75% ethanol, i.e., they were treated with 0.1 N NaOH for 48 hours, and the alkali excess then titrated with 0.1 N HCl. In Fig. 2 absorption curves are presented for lactone titration products of both glycosides. Quite evident is the increase of absorption intensity and displacement of the maximum at 3000 Å to 3550 Å. It should be mentioned that the absorption spectrum for an alkaline solution of corelborin K (before acidification) had an analogous maximum. Similar change in absorption spectra speaks for the fact that under the influence of alcoholic alkali, for the conditions indicated, non-reversible transformation of the unsaturated six-membered lactone ring evidently takes place. This was confirmed by biological tests of the lactone titration product, which was found to be biologically inactive.*

A similar phenomenon was also observed upon polarographic investigation of strophantidine [6], where the action of a 0.03 N-solution of $(\text{CH}_3)_4\text{NOH}$ did not lead to an irreversible formation of non-reducible isoform of strophantidine at the dropping-mercury electrode, but the action of 0.1 N-solution led to formation of the isoform in 15 hours, which, upon acidification, did not change to the original compound. It is characteristic that the absorption curve for the alkaline reaction product of strophantidine (following acidification of the solution) was shifted relative to the strophantidine curve itself toward the long waves, as with corelborin K and corelborin P.

The chief method for quantitative determination of cardiac glycosides up to the present time has been the biological method. This is more with respect to glycosides possessing the six-membered lactone ring, since more or less satisfactory colorimetric methods are available [7] for glycosides with the five-membered ring. In this regard the authors decided to use the absorption spectra for quantitative determination of corelborin K. Inasmuch as it is liberated as a solution in 0.4% chloroethone solution, it was determined that a 0.4% solution of chloroethone* is optically transparent in the spectral range of interest as the result of which qualitative determination of glycoside is possible directly in this solution.

As the result of photographic recording of absorption curves for a number of corelborin K solutions of known concentrations in 0.4% chloroethone, several standard straight lines (for various λ) (Fig. 3) were obtained. For quantitative determination, the straight line 3 was chosen (at 3000 Å), corresponding to that wave length where change in $\Delta \log K / \Delta \lambda$ is small, inasmuch as the probability of experimental error in measurement for constructing the absorption curves is smallest in this range. By means of this straight line a quantitative determination of corelborin K was carried out in a solution of known concentration (see Table).

Quantitative Analysis of an Ampouled Solution of Corelborin K

Quantity of substance taken (for 10 ml of solution, in mg)	Wave lengths								
	3000 Å			3100 Å			3200 Å		
	Found	Diff-erence	Error (%)	Found	Diff-erence	Error (%)	Found	Diff-erence	Error (%)
0.595	0.600	0.005	0.84	0.600	0.005	0.84	0.550	-0.045	-7.60
0.475	0.460	-0.015	-3.20	0.425	-0.050	-10.5	0.400	0.075	15.80
0.370	0.380	0.01	2.70	0.365	-0.005	-1.40	0.400	0.030	8.10

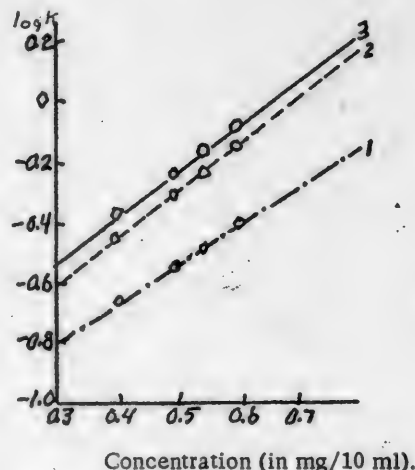


Fig. 3. Standard curves for quantitative determination of corelborin K.
1) 3200 Å; 2) 3100 Å; 3) 3000 Å.

Thus, for more accurate analysis, the absorption spectra should be taken at 0.02 unit intervals on the log K scale. At the same time, while carrying out serial analyses, there is no need to take all of the curve, for it can be limited to that section selected for the calculated wave length range.

SUMMARY

1. Absorption curves for the new cardiac glycosides containing the six-membered lactone ring, isolated from domestic material, have been obtained.

* Glycosides with a ruptured lactone ring are usually found to be biologically inactive.

** "Chloroethone" = $\text{C}_6\text{H}_7\text{OCl}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ (acetone-chloroform) and is added as a preservative to the ampouled solutions.

2. It has been found upon prolonged action of alkaline solution on corelborin K and corelborin P, that they undergo irreversible transformation into biologically-inactive products which possess absorption spectra differing sharply from the glycoside spectra themselves. This phenomenon can be used to detect glycoside transformation products in mixture with glycosides, and qualitative reactions also give a positive result.

3. Quantitative determination of corelborin K in ampouled solutions has been carried out by the use of absorption spectra.

4. The difference between absorption spectra for cardiac glycosides of the digitalic -strophantic and scil-larene groups can be used as a reliable method for determining to which of two groups cardiac glycosides belong.

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Received January 9, 1953.

Kharkov Scientific Research Chemico-
Pharmaceutical Institute.

• See Consultants Bureau Translation, page 155.

A STUDY ON FURANE COMPOUNDS

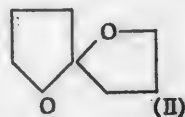
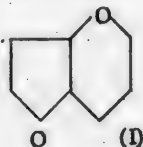
III. THE STRUCTURE OF 1,6-DIOXASPIRO-(4,4)-NONANES AND THEIR FORMATION MECHANISM

A. A. Ponomarev, V. A. Afanasyev and N. I. Kurochkin

It has been mentioned earlier [1] that hydrogenation of furane aldehydes and ketones is accompanied by the formation of bicyclic, non-hydroxylated compounds, along with the corresponding alcohols.

The problem of the structure for these compounds has already been investigated in the special literature.

Adkins and Burdick [2], having discovered for the first time similar compounds among the hydrogenation products of furalacrolein by the use of Raney nickel (NIR), assumed the presence of a 1,5-dioxaoctahydrindene structure, i.e., Formula (I), based upon the absence of characteristic acetal reactions for this compound. In their following work [3], these authors indicated a change in their point of view, because of the identity of this product with the compound obtained at the end of the last century by Fittig [4] from butyrolactone, and which was named by him oxetone, from the latter of which, by the action of HI was formed diiodopropylketone and from the latter dipropyl ketone was formed by reduction, which is in complete accord with the properties that Fittig found for his compound. All of this has led to the thought that the compound forming by hydrogenation of furalacrolein in actuality has the spirane structure corresponding to Formula (II):



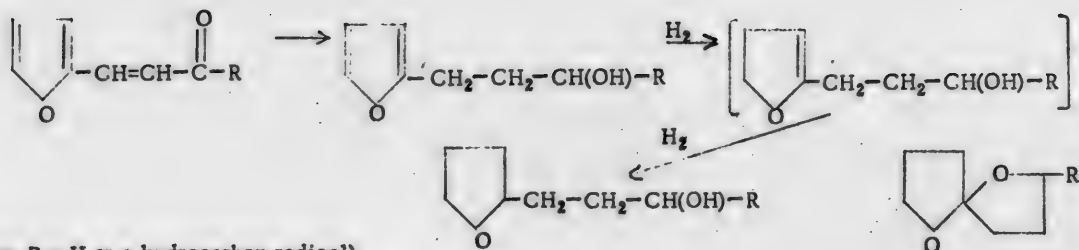
Later, the product was obtained in better yield by hydrogenation of furalpropanol in the presence of nickel on kieselguhr [5].

The structure for the nearest homolog of this spirane — 2-methyl-1,6-dioxaspiro-(4,4)-nonane — which is formed by hydrogenation of furfurylideneacetone over NIR [6], or of furalbutanol over Ni on kieselguhr [5], was confirmed as in the preceding case by its conversion upon heating with HI into diiodoketone, and by reduction of the latter to octanone-4 [5].

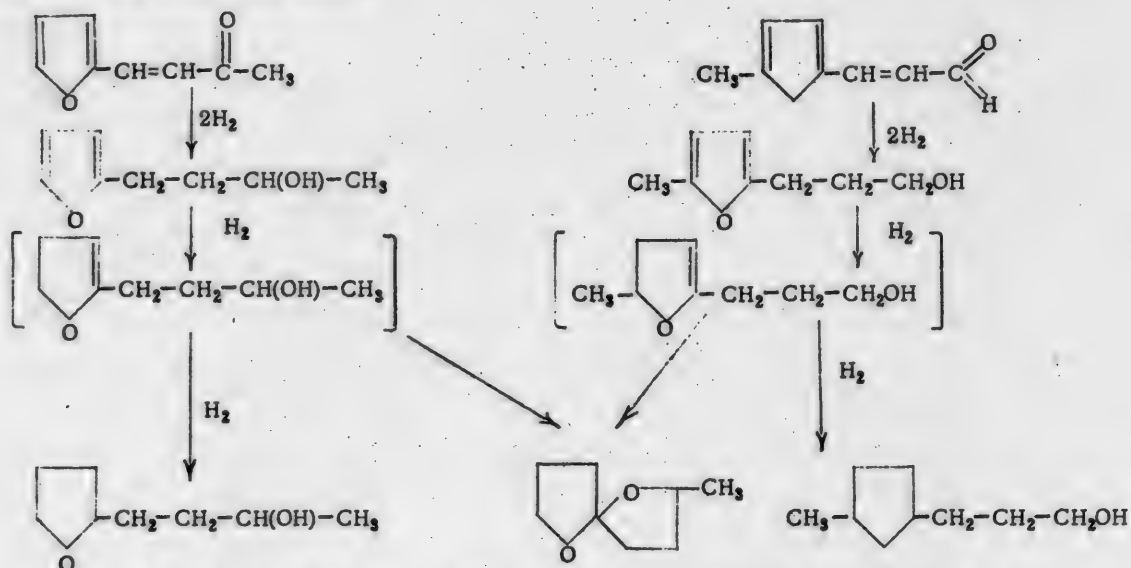
There has also appeared information in the literature on the formation of the analogous bicyclic products from hydrogenation of difurfurylideneacetone [7], α -ethyl- β -(α -furyl)acrolein [6] and α -methyl- β -(α -furyl)acrolein [8]. However, in the latter instances, the authors have not sufficiently substantiated the structures of the products obtained. Furthermore, Hinz, Meyer and Schucking [6] in their article on the formation of bicyclic products by hydrogenation of furalacrolein, furfurylideneacetone and α -ethyl- β -(α -furyl)acrolein, again attribute to them the structure of the cyclic dioxaoctahydrindene.

Though the analytical proofs given earlier [3, 5] for the simplest spirane structure, and its methyl homolog, are sufficiently convincing, nevertheless it should be mentioned that a new synthetic proof for 1,6-dioxaspiro-nonanes can be predicted, based upon the hydrogenation of certain furane aldehydes and ketones. This is possible on the basis of silvane hydration, which is similar to hydrogenation and which is similar to the concept of the spirane formation mechanism: (see next page)

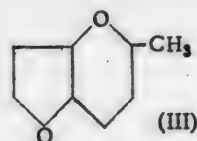
It is not difficult to see that in the case of a similar reaction mechanism, hydrogenation of two compounds — furfurylideneacetone and 3-(2'-methyl-5'-furyl)propen-2-al — should lead to formation of one and the same bicyclic product — 2-methyl-1,6-dioxaspiro-(4,4)-nonane.



(where R=H or a hydrocarbon radical).



According to the reaction mechanism (formation of dioxaspiro-octahydrindene derivatives) two isomeric compounds (III and IV) should result from the above-indicated furane compounds:

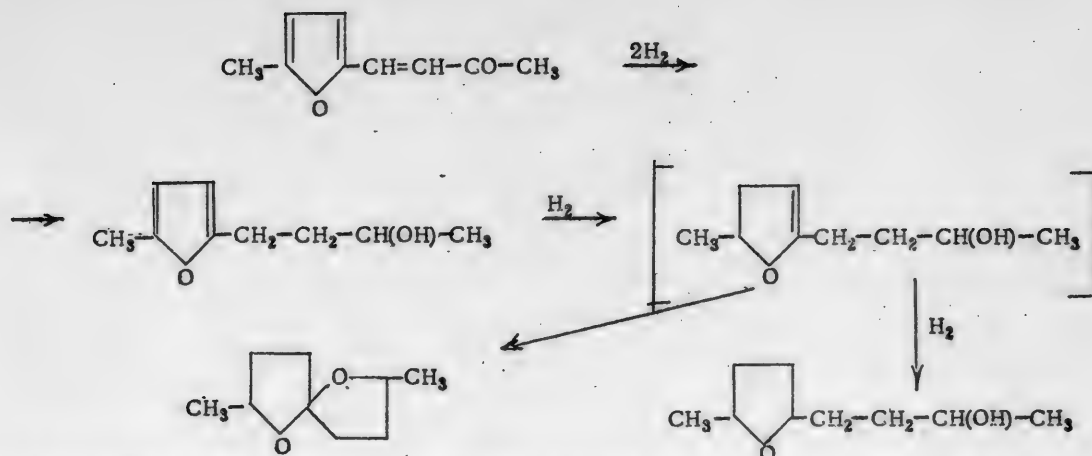


Consequently, the synthesis of 2-methyl-1,6-dioxaspiro-(4,4)-nonane from 3-(2'-methyl-5'-furyl)-propen-2-al is a confirmation of both the identity of five-membered rings in molecules of similar compounds, possibly only for the spirane structure, and of the above-given reaction mechanism.

Apparently, in the case of the above-indicated hydrogenation mechanism for 4-(2'-methyl-5'-furyl)-butene-3-one-2, there may also result an accompanying formation of 2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane, identical with the so-called dimethyloxetone of Fittig obtained from valerolactone [9, 10] and acetonedicarboxylic acid [11]. (see next page).

2,7-Dimethyl-1,6-dioxaspiro-(4,4)-nonane synthesized by such a procedure would be a second representative of this group of compounds obtained from both the furan compound and lactones.

The authors' experiments on two-stage hydrogenation are presented in the present work for 3-(2'-methyl-5'-furyl)-propene-2-al and 4-(2'-methyl-5'-furyl)-butene-3-one-2, as the result of which it has been possible to isolate the corresponding spirocyclic products, identified, respectively, with the spiranes formed by hydrogenation of



furfurylideneacetone, (2-methyl-1,6-dioxaspiro-(4,4)-nonane and the dimethyloxetone of Fittig [2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane]. Thus, may be considered as experimentally confirmed the earlier-expressed concept concerning spirane structure and their formation mechanism from the corresponding furane aldehydes and ketones or γ -(2-furyl)-alkanols. There have also been obtained the following compounds which have not been described in the literature before, information on which is contained in the experimental part: 3-(2'-methyl-5'-furyl)-propen-2-al, 3-(2'-methyl-5'-furyl)-propanol-1, 3-(2'-methyl-5'-tetrahydrofuryl)-propanol-1, 4-(2'-methyl-5'-furyl)-butanol-2 and 4-(2'-methyl-5'-tetrahydrofuryl)-butanol-2.

EXPERIMENTAL

Hydrogenation was carried out in a steel rotating autoclave, with a capacity of 150 ml. The given temperature was maintained by means of an electronic-controlled millivoltmeter.

Catalysts: copper chromite was prepared by the usual method [12], nickel on kieselguhr, an industrial catalyst of domestic production. The catalyst, before use, was powdered to a fine powder and reduced by heating in a stream of hydrogen.

Hydrogenation of 3-(2'-methyl-5'-furyl)-propen-2-al*

This reaction was run by condensing 5-methylfurfural [13] with acetaldehyde, according to a method similar to that for producing furalacrolein [14].

In a typical experiment, 35 g of freshly-distilled 5-methylfurfural was added to a solution of 2.2 g of NaOH in 500 ml of water, cooled to 0°, over a period of 10 minutes, after which a solution of 21 g of acetaldehyde in 100 ml of water was added over a period of 3-4 hours. Stirring of the reaction mixture was continued for another 2 hours, and then neutralized with the calculated amount of acetic acid. The product was extracted with three portions of ether, 100 ml each, the ether extract dried with anhydrous sodium sulfate, and the residue, after removal of ether, distilled in vacuo. Upon repeated distillation, 11.5 g (28% of theory) of product was obtained, boiling at 98-100° (4 mm). A yellowish oil with peculiar odor.

0.2104 g substance: 0.5406 g CO₂; 0.1176 g H₂O. 0.2024 g substance: 0.5210 g CO₂; 0.1155 g H₂O.
Found %: C 70.23, 70.25; H 6.25, 6.38. C₈H₈O₃. Calculated %: C 70.57; H 5.92.

Semicarbazone: white, well-developed needles, m.p. 191°.

3-(2'-Methyl-5'-furyl)propen-2-al condenses with ketones, similarly as with furalacrolein. Thus, for example, upon condensing two moles of aldehyde with cyclohexanone, the ketone C₂₂H₂₂O₃ is formed, orange crystals with m.p. 168-168.5°.

0.1050 g substance: 0.3024 g CO₂; 0.0648 g H₂O. 0.1188 g substance: 0.3486 g CO₂; 0.0722 g H₂O.
Found %: C 78.59, 78.70; H 6.91, 6.80. C₂₂H₂₂O₃. Calculated %: C 79.01; H 6.63. Found: M 345.8.
Calculated: M 334.4.

* M. D. Lipanova participating.

3-(2'-Methyl-5'-furyl)-propanol-1

18 g of 3-(2'-methyl-5'-furyl)-propen-2-ol, 40 ml of absolute alcohol and 3 g of copper chromite catalyst were placed in the autoclave. The initial hydrogen pressure was 135 atm. the temperature 120°. Hydrogenation was complete after absorption of 5850 ml of H₂ (2 moles). After removal of catalyst and alcohol, the hydrogenate was distilled in vacuo. Upon repeated distillation of the product, the fraction with 97-98°, b.p. at 8 mm was collected. Yield was 75% of theory. Colorless liquid with faint odor, readily-soluble in alcohol and ether.

n_D^{20} 1.4775; d_4^{20} 1.0322; MR_D 38.42; calculated 39.17.

0.0915 g substance: 0.2285 g CO₂; 0.0682 g H₂O. 0.0873 g substance: 0.2184 g CO₂; 0.0665 g H₂O.
Found %: C 68.15, 68.27; H 8.34, 8.53. C₈H₁₂O₂. Calculated %: C 68.52; H 8.62. Found %: OH 10.0.
Calculated %: OH 12.0. Found: M 142, 147. Calculated: M 140.

3-(2'-Methyl-5'-tetrahydrofuryl)-propanol-1 and 2-methyl-1,6-dioxaspiro-(4,4)-nonane

24 g of 3-(2'-methyl-5'-furyl)-propanol-1, 40 ml of absolute alcohol and 1.2 g of catalyst (nickel on kieselguhr) were charged into the autoclave. The initial hydrogen pressure was 150 atm. The hydrogenation temperature was 120°. Hydrogenation was terminated after absorption of about 1.5 moles of hydrogen (5200 ml). After the usual treatment, the catalysate was distilled in vacuo at 46 mm and the low-boiling fractions collected (up to 110°), plus a fraction with b.p. 111-113°, weighing 15.3 g (yield 63.5%), representing methyltetrahydrofurylpropanol. A colorless liquid with faint odor.

n_D^{20} 1.4635; d_4^{20} 0.9972; MR_D 39.87; calculated 40.11.

0.1020 g substance: 0.2480 g CO₂; 0.922 g H₂O. Found %: C 66.35; H 11.15. C₈H₁₂O₂. Calculated %: C 66.62; H 11.18. Found: M 147, 150. Calculated: M 144.2. Found %: OH 11.88. Calculated %: OH 11.80.

To increase the product, the experiment was repeated under the same conditions with the same amounts of initial alcohol, solvent and catalyst.

The low-boiling fractions of both experiments, as well as the residue after repeated distillation through an efficient fractionating column of the solvent distilled off from the catalyzate were combined and redistilled through the fractionating column at atmospheric pressure, as the result of which 7.5 g of fraction, with b.p. 162-164°, was isolated (yield was 15.6% of theory).

Found: M 140.0, 136.8. Calculated: M 142.19. n_D^{25} 1.4412; n_D^{20} 1.4428; d_4^{20} 0.9920; MR_D 37.99; calculated: 38.08.

According to the literature data [5, 6]: 2-methyl-1,6-dioxaspiro-(4,4)-nonane had the following physical constants: n_D^{25} 1.4412; d_4^{25} 0.985; b.p. 157-159°, 80° at 45 mm.

Hydrogenation of 4-(2'-Methyl-5'-furyl)-buten-3-one-2

4-(2'-Methyl-5'-furyl)-buten-3-one-2 was obtained by condensing 5-methylfurfural with acetone in the presence of NaOH [15], b.p. 105.5-107° at 4 mm, m.p. 35-36°. Yield was 61.1% of theory.

4-(2'-Methyl-5'-furyl)-butanol-2

In a typical experiment, 28.5 g of 4-(2'-methyl-5'-furyl)-buten-3-one-2, 40 ml of absolute alcohol and 3 g of copper chromite catalyst were charged into the autoclave and hydrogenated at 120° and an initial hydrogen pressure of 88-95 atm. For accumulation of material, hydrogenation was carried out 5 times for a total amount of 129.9 g of initial ketone. The combined catalyzate from 5 experiments was freed from catalyst and solvent, and then distilled in vacuo at 55 mm. 107.5 g of product resulted, boiling at 136.5-138°, a colorless liquid with faint odor, miscible with standard organic solvents. Yield was 80.5%.

n_D^{20} 1.4760; d_4^{20} 1.000; MR_D 43.49; calculated 43.80.

0.0662 g substance: 0.1706 g CO₂; 0.0559 g H₂O. 0.1732 g substance: 0.4458 g CO₂; 0.1443 g H₂O.
Found %: C 70.26, 70.20; H 9.45, 9.32. C₉H₁₄O₂. Calculated %: C 70.09; H 9.15.

Found: M 154.7. Calculated: M 154.2. Found %: OH 11.8, 11.7. Calculated %: OH 11.03.

4-(2'-Methyl-5'-tetrahydrofuryl)-butanol-2 and 2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane.

91.7 g of 4-(2'-methyl-5'-furyl)-butanol-2 was hydrogenated four times for a total of 4.7 g of copper chromite catalyst and 184 ml of absolute alcohol. The initial hydrogen pressure was 130-145 atm. The temperature was 120°.

The combined catalyzate from 4 experiments was freed from catalyst and solvent and then redistilled in vacuo at 46 mm. 8.65 g of the substance resulted, boiling at 130°, and the main fraction with b.p. 134-136°, weighing 69.35 g (73.6% of theory), which was found to be 4-(2'-methyl-5'-tetrahydrofuryl)-butanol-2. Upon repeated distillation, the boiling point of the product remained constant.

n_D^{20} 1.4542; d_4^{20} 0.9574; MR_D 44.76; calculated 44.73.

0.0770 g substance: 0.1938 g CO_2 ; 0.0773 g H_2O . 0.0956 g substance: 0.2401 g CO_2 ; 0.0959 g H_2O . Found %: C 68.48, 68.48; H 11.24, 11.16. $C_9H_{12}O_2$. Calculated %: C 68.31; H 11.47. Found: M 169.2. Calculated M 158.2. Found %: OH 11.27. Calculated %: OH 10.74.

The low-boiling fraction was redistilled at atmospheric pressure. Because it was not possible to narrow down the boiling range (168-175°) of the small fraction, despite repeated distillation, the boiling point of the product was more precisely determined according to Emich [16], and was found to be 167-169°. Weight was 2.87 g.

n_D^{20} 1.4389; d_4^{20} 0.9594; MR_D 42.82; calculated 42.65.

0.1215 g substance: 0.3070 g CO_2 ; 0.1111 g H_2O . 0.1192 g substance: 0.3001 g CO_2 ; 0.1099 g H_2O . Found %: C 68.92, 68.66; H 10.23, 10.32. $C_9H_{12}O_2$. Calculated %: C 69.19; H 10.32. Found: M 149.5. Calculated: M 156.2.

The product did not show the presence of hydroxyl groups; it gave a silver mirror with an ammoniacal silver oxide solution. It formed white crystals with hydrogen bromide, m.p. 41-42°, and possessed a very pleasant odor.

According to the literature data [9, 10]: the Fittig dimethyloxetone has a b.p. of 169.5°; 167-169°; d_4^{20} 0.978; it forms a silver mirror with an ammoniacal solution of silver oxide; it possesses a terpene odor. The interaction product with HBr melts at 42°.

SUMMARY

1. As the result of catalytic hydrogenation of 3-(2'-methyl-5'-furyl)-propene-2-al and 4-(2'-methyl-5'-furyl)-butene-3-one-2 there have been obtained 3-(2'-methyl-5'-furyl)-propanol-1, 3-(2'-methyl-5'-tetrahydrofuryl)-propanol-1, 4-(2'-methyl-5'-furyl)butanol-2 and 4-(2'-methyl-5'-tetrahydrofuryl)-butanol-2, as well as 2-methyl-1,6-dioxaspiro-(4,4)-nonane and 2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane.

2. It has been demonstrated that the formation of 2-methyl-1,6-dioxaspiro-(4,4)-nonane from 3-(2'-methyl-5'-furyl)-propene-2-al by catalytic hydrogenation constitute a new synthetic proof, both of the structure for spiranes of this type, and for their formation mechanism from furfurylidene aldehydes and ketones and γ -(2-furyl)-alkanols as accepted by the authors.

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Received January 6, 1953

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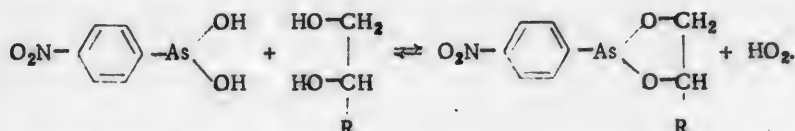
* See Consultants Bureau English Translation, p. 663.

α-GLYCOLIC ESTERS OF p-NITROPHENYL-ARSENOUS AND α-NAPHTHYL-ARSENOUS ACIDS

Gilm Kamai and N. A. Chadaeva

The present work is a continuation of the authors' investigations in the field of cyclic glycolic esters of arsenous and arylarsenous acids. Here work has been undertaken to study the method of synthesis of certain cyclic α-glycolic esters of p-nitrophenyl-arsenous and α-naphthyl-arsenous acids.

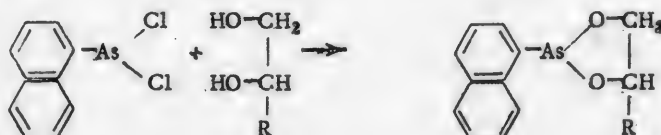
By action of an equimolecular quantity of p-nitrophenylarsenous acid upon various α-glycols (with heating), α-glycolic esters of p-nitrophenylarsenous acid were synthesized according to the following equation:



where: R=H or CH₂OCH₃, CH₂OC₂H₅.

Thus, the ethyleneglycolic, α-methoxypropyleneglycolic and α-ethoxypropyleneglycolic esters of p-nitrophenylarsenous acid were isolated, readily hydrozable by water.

The α-glycolic esters of α-naphthylarsenous acid were obtained by the authors through the interaction of α-naphthyldichloroarsine with the corresponding α-glycols in absolute ether medium with the presence of pyridine, according to the equation:



The resulting α-glycolic ester of α-naphthylarsenous acid was a viscous, transparent liquid, unstable in the air, hydrolyzing to form α-naphthylarsineoxide.

EXPERIMENTAL

Synthesis of the Ethyleneglycolic Ester of p-Nitrophenylarsenous Acid

13 g of vacuum-distilled p-nitrophenylarsenous acid and 12 g of freshly-distilled ethylene glycol were placed in an Arbuzov distilling flask. The apparatus was put under vacuum, and the flask contents then carefully heated on an oil bath. Drops of reaction water were observed on the walls of the flask at a bath temperature of about 80°. The distillation was carried out at constant vacuum. Two fractions were isolated:

1st, B.p. 98-100° at 12 mm - 7.2 g; 2nd, B.p. 170-174° at 5 mm - 7.8 g.

The second fraction solidified upon standing. After recrystallization from carbon tetrachloride, the crystals melted at 119-121°.

Found %: As 28.89, 28.93. C₈H₇O₄AsN. Calculated %: As 29.14.

The resulting ester was represented as light-yellow crystals, readily soluble in diverse organic solvents; hydrolyzed by water, forming p-nitrophenylarsenous acid.

Synthesis of the α-Methoxypropyleneglycolic Ester of p-Nitrophenylarsenous Acid

13.6 g of the compound was obtained, with b.p. 188-190° at 2 mm (with partial decomposition) from a mixture of 22 g of α-methoxypropyleneglycol and 21.3 g of p-nitrophenyl-arsenous acid in a manner similar to that described above.

Found %: As 25.15, 25.08. $C_{10}H_{12}O_5AsN$. Calculated %: As 24.88.

The ester obtained was represented by light-yellow, hygroscopic crystals, with m.p. 54-55°, readily in organic solvents. It was readily hydrolyzed by water.

Hydrolysis of the α -Methoxypropyleneglycolic Ester of p-Nitrophenylarsenous Acid.

3 g of the ester under investigation was dissolved in 15 ml of 20% sodium hydroxide. The solution was filtered off and neutralized with 15% hydrochloric acid. The precipitated fine yellow crystals were filtered off and washed repeatedly with water. After drying to constant weight, the crystals were analyzed.

Found %: As 32.38, 32.53. $C_8H_8O_4AsN$. Calculated %: As 32.42.

The crystals were found to be p-nitrophenylarsenous acid.

Synthesis of the α -Ethoxypropyleneglycolic Ester of p-Nitrophenylarsenous acid.

The ester was obtained by interacting 10 g of p-nitrophenylarsenous acid with 14 g of α -ethoxypropyleneglycol. B.p. 184-185° at 3 mm. The yield of pure compound was 5.2 g.

Found %: As 23.51, 23.64. $C_{11}H_{14}O_5AsN$. Calculated %: As 23.87.

The ester was a yellowish-green, viscous liquid, readily soluble in the standard solvents:

d_4^{20} 1.4793; n_D^{20} 1.5700. Found: MR_D 70.49. $C_{11}H_{14}O_5AsN$. Calculated: MR_D 68.36.

It was hydrolyzed by water to form the original compounds.

Synthesis of the Ethyleneglycolic Ester of α -Naphthylarsenous Acid.

14 g of α -naphthylidichloroarsine dissolved in 100 ml of ethyl ether was added through a dropping funnel, with stirring, to a solution, pre-cooled to 0°, of 4 g of ethylene glycol and 7.9 g of anhydrous pyridine in 350 ml of absolute ether. Having introduced the total amount of α -naphthylidichloroarsine, the flask contents were then heated on a water bath for 30 minutes. After cooling, the precipitate of pyridine hydrochloride was filtered off, washed with ether, the solvent distilled off, and the remaining liquid fractionated in vacuo. 5.55 g of the compound, with b.p. 169-170° at 4 mm resulted.

Found %: As 28.44, 28.65. $C_{12}H_{11}O_2As$. Calculated %: As 28.65.

The ester was a transparent, viscous liquid, soluble in the usual organic solvents. It was readily hydrolyzed by water to form α -naphthylarsineoxide.

d_4^{20} 1.5043; n_D^{20} 1.6677.

Synthesis of the α -Methoxypropyleneglycolic Ester of α -Naphthylarsenous Acid

This compound was isolated by the method described above, proceeding from the corresponding α -glycol, 7.9 g of dry pyridine, 400 ml of ethyl ether, and 14 g of α -naphthyl-dichloroarsine. The b.p. was 185-186° at 3 mm. Yield was 7 g.

Found %: As 24.15, 24.21. $C_{14}H_{15}O_3As$. Calculated %: As 24.47.

The ester — a viscous, transparent liquid: d_4^{20} 1.4209, n_D^{20} 1.6282. Hydrolyzing in moist air to form α -naphthylarsineoxide, with m.p. 245°.

SUMMARY

1. Various α -glycolic esters of p-nitrophenylarsenous and α -naphthylarsenous acids were synthesized and some of their properties have been studied.

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Received June 22, 1953

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